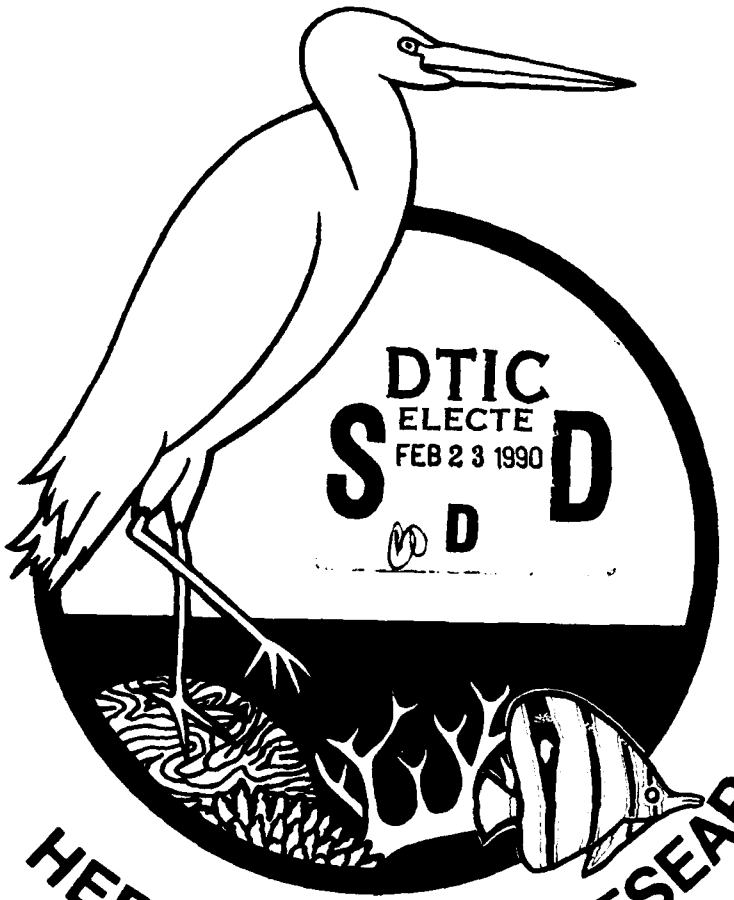
(1)

MARINE BIOINORGANIC CHEMISTRY

28 th JUNE - 2nd JULY 1989



HERON ISLAND RESEARCH STATION

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DEPARTMENT OF CHEMISTRY

BERKELEY, CALIFORNIA 94720
FAX: (415) 642-8369

February 9, 1990

Dr. Harold Bright
Office of Naval Research
Code 1141MB
800 North Quincy Street
Arlington, VA 22217-5000

Dear Dr. Bright:

This letter will accompany the final report for Grant Number N00014-89-J-3006 in the amount of $5,000 for the period June 14, 1989 through June 13, 1990. These funds were for the project entitled "A Proposal to Support Participants of the Symposium Accompanying the Marine Bioinorganic Chemistry Workshop to be Held on Heron Island, Wednesday, June 28 through Sunday, July 2, 1989."

The workshop itself was supported by the U.S./Australia Science and Technology Agreement through the National Science Foundations of the two respective countries. This ONR grant was intended to provide support for graduate students, postdoctoral fellows and some faculty to attend the symposium which accompanied the workshop. Enclosed is an article written by Professor Frances Ann Walker, an attendee of the meeting, who acted as secretary for the meeting and provided an article to the American Chemical Society Bioinorganic Subdivision Newsletter. Copies of that report are enclosed as the scientific report of this grant.

Travel funds were provided for the following individuals with their institutional affiliations, professional title, and dollar support amounts indicated:

Symposium Attendee	Institution	Position	Travel Support Provided
Peter Ford	*UC Santa Barbara*	*Professor of Chemistry*	$1,200
Elizabeth Theil	North Carolina State Univ.	Professor of Biochemistry	$1,400
Donald Kurtz	University of Georgia	Assoc. Prof. of Chemistry	$ 900
de la Rosa	UC Santa Barbara	Graduate Student	$ 500
Reid	UC Santa Barbara	Graduate Student	$ 500
Soedjak	UC Santa Barbara	Graduate Student	$ 500

Also attached is a copy of the cumulative detail report provided by the College of Chemistry Accounting Office showing the above expenditures and the final zero balance.

We appreciate the support of the ONR for this most successful workshop and symposium.

Sincerely,

Kenneth N. Raymond
Professor of Chemistry

KNR:ss

Enclosures

ACCOUNT ADMINISTRATOR: BREWER, LARRY A.

PRINCIPAL INVESTIGATOR	AGENCY NAME/NUMBER	ACCOUNT-FUND	COST CENTER	AWARD PERIOD
RAYMOND, KENNETH N.	ONR	441230-23061	7125	06/14/89-06/13/90

SUB OBJ	VENDOR	P.O. #	TAG #	DESCRIPTION	DOCUMENT DATE	APPROPRIATIONS	EXPENDITURES	LIENS	ESTIMATES
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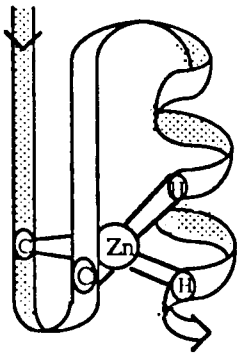
	2901 TRAVL			FORD; MARINE BIOINORGANI	08/03/89		1,200.00		
	2901 TRAVL			THEIL; MARINE BIOINOR CH	08/03/89		1,400.00		
	2901 TRAVL			KURTZ; MARINE BIOINOR CH	08/03/89		900.00		
	2901 TRAVL			DE LA ROSA-HERON ISLAND,	08/03/89		500.00		
	2901 TRAVL			REID-HERON ISLAND, AUSTR	08/08/89		500.00		
	2901 TRAVL			SOEDJAK; MARINE BIOINOR	08/08/89		500.00		
	CURRENT MONTH ACTIVITY					5,000.00	5,000.00		
	SUBTOTAL PARTICIPANT SUPPORT					5,000.00	5,000.00		
	AVAILABLE FUNDS			.00 ***					
	DIRECT COST TOTAL					5,000.00	5,000.00		
	AVAILABLE FUNDS			.00 ***					
	TOTAL COST CENTER - 7125					5,000.00	5,000.00		
	AVAILABLE FUNDS			.00 ***					



A.C.S.
Bioinorganic Subdivision
Newsletter

WINTER 1989

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Bernhard Lippert
Thomas Tullius
F. Ann Walker
Helmut Sigel, European Editor

Australian Conference on Marine Bioinorganic Chemistry

F. Ann Walker
Chair-elect, Bioinorganic Subdivision
Department of Chemistry and Biochemistry, San Francisco State Univ., San Francisco, CA 94132

The conference on Marine Bioinorganic Chemistry was held on Heron Island on the Great Barrier Reef off Gladstone, Queensland, from June 28 to July 2, 1989. Approximately one hundred scientists from around the world attended. Organizers of the conference were Clifford J. Hawkins and Margo Balfour, University of Queensland, and Kenneth Raymond, Berkeley. Financial support for the conference came from the US/Australia Cooperative Science Program from the Australian Department of Industry, the US National Science Foundation, the Queensland Premier's Department, the US Office of Naval Research, and a number of corporate sponsors. Delegates and their guests stayed either at the University of Queensland's Heron Island Research Station (HIRS) or at the Heron Island Resort; conference sessions were held in the Resort's Pandanus Lounge. Laboratory work was conducted in the laboratories of HIRS, with instrumental capabilities augmented for the occasion by the Australian branches of Pharmacia, Varian, and Beckman Instruments.

The three and one-half day meeting was organized in such a way as to maximize the time available during daylight hours for collecting specimens and conducting laboratory work or just exploring the island and reef by foot or by snorkeling or diving, while the formal conference sessions were held in the late afternoons and evenings. The seven conference sessions are summarized below:

(1) The Ocean and Seas: A welcome and overview by Cliff Hawkins was followed by Francois Morel (MIT), who gave a survey of trace metals and phytoplankton in the sea, and Alan Bond (Deakin University), who discussed the quantification and speciation of metals in the sea. Dr. Bond pointed out the serious sampling problems and ease of contamination of marine samples, and the need to develop new technology that could make non-invasive measurements with the information content of NMR spectroscopy at the concentration levels accessible to electrochemical techniques. He stated that he thought that most of the available trace metal concentration and speciation data are in error.

(2) Arsenic Chemistry of Marine Organisms and Biomineralization: Kevin Francesconi (Western Australia Marine Research Laboratories) and Bill Cullen (University of British Columbia) discussed the organoarsenicals that are found in marine organisms. Both Australian and New England lobsters, as well as many fish, contain fairly high concentrations of arsenobetaine ($Me_3As^+CH_2COO^-$) which may come up the food chain from symbiotic coral algae (zooxanthelle) or seaweed, both of which make a number of arsenyl-ribosides. However, to date it has not been possible to prove the enzymatic conversion of the $Me_2As(O)CH_2CH_2OH$ degradation product of the arsenyl-ribosides to the trimethylarsonium group found in arsenobetaine. There is no known requirement for arsenic in living systems, so the biosynthesis of the arsenyl-ribosides appears to be the algae's way of coping with this heavy main group element that is fairly abundant in marine waters.

Dennis Chasteen (University of New Hampshire) then discussed calcification in the exoskeletons of bivalve mollusks, which form calcite and/or aragonite in a highly ordered microstructure in intimate association with an organic matrix, and John Webb (Murdoch University) discussed the complex process of biomineralization of iron in the teeth of chitons and limpets. The iron appears to be supplied by ferritin, from which Fe(II) is released. As the iron is deposited in new teeth, it goes through a series of hydrous iron oxide/hydroxide forms and is finally transformed into magnetite (Fe_3O_4) in the hardest parts of the teeth.

(3) Marine Algae: Talks were given by Alison Butler (University of California, Santa Barbara), Ron Wever (University of Amsterdam), and Hans Vilter (Friederich Wilhelms University) on vanadium (and non-heme iron) haloperoxidases. These enzymes halogenate a wide variety of organic compounds in the absence of heme. Butler pointed out that dioxygen is a byproduct of the reaction and suggested that it is produced as singlet oxygen. She and the other two speakers left open the question of what the actual brominating species is. Wever stressed that in his experience the enzyme as isolated contains less than one mole of vanadium, although it can be reconstituted with VO^{3-}. He also has investigated the oxidation state of vanadium by EXAFS and EPR and concludes that the native enzyme has V(V) with a predominance of O and N ligands, one of which is probably histidine and one tyrosine, and that V(V) serves only as a binding site for Br^- and H_2O_2 (i.e., V(IV) is not involved in the catalytic cycle). Vilter reported finding vanadium bromoperoxidase in a wide variety of brown algae from various parts of the world, but not in red or green algae, fungi or lichens. ^{51}V NMR spectroscopy and EXAFS suggest mainly oxygen ligands. Crystals obtained for a bromoperoxidase from a brown seaweed found in northern latitudes diffract at 2.8 Å. Peter Ford (University of California, Santa Barbara) then discussed inorganic photochemistry in general terms, and Vincent Pecoraro (University of Michigan) discussed possible models for the manganese center of the photosynthetic water oxidizing system of algae.

(4) The Ascidians: Talks were given by Ken Kustin (Brandeis University), Jim Swinehart (University of California, Davis) and Cliff Hawkins (University of Queensland) on the vanadium- and iron-containing blood cells of these sedentary chordates, which in some cases concentrate vanadium up to 1 M, or about a factor of 10^7 over its concentration in sea water. Kustin emphasized the large number of different types of blood cells in ascidians and the need to sort the cells in order to obtain meaningful results. Swinehart emphasized the major differences in membrane composition of the branchial sacs of various species and how this correlates with vanadium uptake, while Hawkins reported the isolation of a DOPA-protein called ferreascidian from the blood cells of *Pyura stolonifera* (an iron-containing ascidian) that contains 42% tyrosine and 17% DOPA. $Fe(NTA)^{3-}$ readily binds to this protein to form four Fe(NTA)(Cat) units. In the aplousbranch and phlebobranch ascidians, which contain high concentrations of vanadium, the blood cells turn a brilliant blue in the presence of 2,2-bipyridyl, showing that the weak V(IV) signal present in freshly obtained cells increases greatly in intensity upon exposure to oxygen. Whole animal ESR spectra following oxidation show two types of V(IV) signals in different sub-orders, suggesting different coordinating ligands for the vanadium binding centers of the different sub-orders. The purpose of the vanadium is as yet unknown.

Following these three talks, Herbert Waite (University of Delaware) gave an interesting talk about adhesives used by mussels, barnacles, oysters, etc. The protein components of these marine bioadhesives have very diverse primary sequences but share high isoelectric points, strong affinities for a variety of metals, and contain DOPA. Molecular weights of many of these proteins exceed 100 kDa. Spectroscopic evidence suggests mono-, bis-, and tris-catecholato complexes with Fe(III).

(5) Marine Iron Proteins: Steve Lippard (MIT) reviewed the structure of the 2-Fe centers of hemerythrin and ribonucleotide reductase and the structures and properties of inorganic compounds prepared to model the 2-Fe sites of these proteins. He then discussed the preparation of models of the 2-Fe centers of methane monooxygenase, which appears to function by "reductive oxidation" (i.e., it is a mixed-function oxidase). These new iron catalysts, derived from $[Fe_2OCl_6]^{2-}$ and ascorbic or tetramethylreductic acid, that utilize O_2 to oxidize hydrocarbons, and the structure of one such complex was presented. Then Karl Wieghardt (Ruhr University) presented a tour-de-force of the preparation and magnetic properties of the first-row transition-metal homo- and heterodimers of the type $LM\{\mu\text{-oxo-bis}(\mu\text{-acetato})\}]M'L'^{n+}$ (n = +2, +3; 1,L' = 1,4,7-triazacyclononane or its N,N',N''-trimethyl analog; M,M' = Fe(III), FE(IV), Mn(III), Mn(IV), Cr(III), V(III), Ti(III)). The purpose of the study was to gain an understanding of the magnetic coupling in these systems. For

example, it was known that the Fe(III)-Fe(III) dimer (and those of Lippard and Armstrong) was strongly antiferromagnetic, while the Mn(III)-Mn(III) dimer was weakly ferromagnetic. When the heterodimer was found to be antiferromagnetically coupled with overall S = 1/2, it was clear that a theory should be developed. With Girerd and co-workers at the Université Paris-Sud, the Wieghardt group carried out a detailed analysis of the interacting magnetic orbitals, revealing that the d_{z^2}-d_{xz} orbital interaction (z is oriented along the M-oxo bond, x bisects the two acetato bridges) is the dominant magnetic path propagating strong antiferromagnetic exchange coupling when the d_{z^2} orbital of one metal and the d_{xz} orbital of the other are half filled (d^5d^5, d^5d^4, d^3d^3, d^1d^1); removal of either or both of these electrons leads to ferromagnetic coupling (d^4d^4, d^4d^3, d^3d^2, d^2d^2).

Keith Murray (Monash University) then discussed structural and magnetic properties of bridged iron(III) phthalocyanine complexes, in which the bridging ion is oxo, imido, sulfido, nitrido, and carbido. The μ-carbido complex is best described as an Fe(IV)-Fe(IV) dimer. After Murray's talk, David Dolphin (University of British Columbia) gave an overview of cytochrome P450 and heme peroxidase chemistry. He pointed out that two of the pigments believed to be formed by such enzymes are Tyrian blue and indigo, both of which are derived from oxidative coupling of indoles. Model hemes that are particularly robust for chemical studies of high valent iron porphyrin oxidation reactions include perchlorotetraphenylporphyrin (chlorinated at both pyrrole and phenyl positions, 28 Cl in all) and tetra-(2,6-dichlorophenyl)porphyrin and its sulfonated analogue. The latter can be used for model studies in aqueous solution.

(6) Copper and Molybdenum Systems: Tony Wedd (LaTrobe University) presented an overview of molybdoenzymes and pointed out their potential importance in the marine environment due to the high concentration of Mo in sea water (100 mM as MoO_4^{2-}). The photosynthetic cyanobacteria (blue-green algae) fix nitrogen utilizing the Mo-Fe enzyme nitrogenase and have been well studied, but the study of oxo-molybdenum enzymes in marine animals, plants, and bacteria is undeveloped. Then Hans Freeman (University of Sydney) gave a short presentation in which he wondered if di-copper and di-iron sites in proteins such as hemocyanin and hemerythrin could have developed by gene duplication of proteins that originally had only one metal site. Then Geoff Sykes (The University, Newcastle upon Tyne) presented a summary of the oxygenation and oxidation of hemocyanin. He began by pointing out that hemerythrin, hemocyanin and myoglobin all have very similar k_{on}, k_{off}, and K_{eq} values for oxygenation. He then discussed oxidation of deoxy-Hc with H_2O_2 and $Fe(CN)_6^{3-}$ (no reaction in the latter case) and reduction of met-Hc with $[Co(sep)]^{2+}$ (also no reaction) in terms of the buried nature of the Hc active site. Then Tom Sorrell (University of North Carolina) discussed synthetic models for the active site of Hc. He first pointed out that while oxy-Hc is believed to have a Cu-O-O-Cu peroxo-bridged structure (from the work of Solomon), in CO-Hc the CO has been shown to bind to only one Cu. However, only one CO will bind. CO-Hc luminesces at 537-556 nm depending on the organism from which it is isolated. Sorrell has made tripodal 2-substituted N-methylimidazole ligands that bind Cu(I) to give a complex that binds CO and luminesces as both precursor and CO adduct. He has also made several bis-imidazole amine ligands that bind Cu(I) as a tridentate ligand. These complexes bind O_2 reversibly at low temperatures to form an intense blue color, but the spectrum is not the same as that of oxy-Hc.

(7) Summary and the Future: Alan Sargeson (Australian National University) commented that F.P.O. (Frank) Dwyer was the father of bioinorganic chemistry in Australia, and that forty years ago he was investigating the biological activity of transition metals and their complexes. He then called upon those who had been carrying out experiments to report on their progress. Alison Butler reported that she and her students had found bromoperoxidase in a species of *Laurencia* and in tunicates, that they had looked at iron uptake by marine bacteria and thought that they probably secreted a siderophore, and that they had looked for lipoxygenase in marine algae. Ron Wever reported finding a bromoperoxidase in a red algae with a molecular weight of about 300 kDa. They do not yet know if it is a vanadium-containing enzyme. Hans Vilter reported that they found no bromoperoxidase in *sargassum* or *tubinaria*, and thus its occurrence might be seasonal. Liz Theil's

(North Carolina State) experiments involved the search for ferritin in phytoplankton and eventual sequencing of that ferritin. Indeed, gels showed the presence of ferritin, so the project will continue. The reason for interest in the amino acid sequence of this ferritin is that it has been found that both higher animals and plants (soybean) have similar ferritin sequences, whereas *E. coli* ferritin is very different; phytoplankton are much more ancient organisms, and thus the relationship of their ferritin to the others would be interesting.

Dick Holm (Harvard) commented that the field of bioinorganic chemistry has now evolved to the point at which specialized conferences such as this one can now be held. He pointed out what he called the "expanded significance of the single result," in which one particular system or result has turned out to have broader significance than originally expected. He cited the cases of hemerythrin, where the detailed information obtained by Don Kurtz and others on the structure, spectroscopic and magnetic properties and chemical reactivity has contributed to our understanding of ribonucleotide reductase and perhaps methane monooxygenase, and plastocyanin, which has contributed to our understanding of cytochrome oxidase. He again mentioned plastocyanin, "poised between Cu(I) and Cu(II)," in reference to the entatic state hypothesis of Williams and Vallee. He sees Fe_3S_4 clusters as similarly poised, ready to take up another iron if the protein would allow it. In terms of the future, he brought up the question of the metal that was not discussed – nickel – and wondered if there were a bioinorganic role for Ni in the marine environment. He also said that he felt that the future of marine bioinorganic chemistry was as unlimited as the number of organisms in the sea, but the problem was to find sources of funding for this new research. Ken Raymond followed a similar theme in saying that marine bioinorganic chemistry is a field with much less development than natural products marine organic chemistry, so there is much room for expansion in the field. He also likened this meeting to the first bioinorganic chemistry meeting, in Blacksburg, VA, in 1970, where there were two communities in attendance – the biochemists and the inorganic chemists. "At the Heron Island meeting we have seen a much wider, more interfacial group, with lectures on topics as diverse as how mussels attach themselves to solid surfaces to the Hamiltonians of spin coupling."

Steve Lippard thanked Ken Raymond for raising the U.S. funds for the meeting, Margo Balfour for the excellent organization of the conference, and Cliff Hawkins for the original idea and for putting it all together. For a meeting that some may have thought had the potential of being simply a lark, the Heron Island meeting was in fact a stimulating and productive scientific meeting that all of the participants will remember for a long time to come. It is safe to predict that there will be a significant increase in the number of scientists who study marine bioinorganic chemistry!

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This grant provided funds to support the participation of U.S. research workers in a symposium that accompanied the "Marine Bioinorganic Workshop" held on Heron Island, Australia, June 28 through July 2, 1989. This ONR grant was intended to provide support for graduate students, postdoctoral fellows and some faculty to attend the symposium which accompanied the workshop.

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MARINE BIOINORGANIC CHEMISTRY WORKSHOP

Under the auspices of the US/Australia Cooperative Science Program

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US National Science Foundation

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2.

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INDEX

ORGANISERS' WELCOME

We are delighted to be able to welcome you to Heron Island to participate in the Marine Bioinorganic Chemistry Workshop. The Workshop has been made possible because of grants under the US/Australia Cooperative Science Program from the Australian Department of Industry, Technology and Commerce, and the US National Science Foundation. We are very grateful for their financial support.

The funds provided under the agreement were not sufficient to cover the costs of the Workshop and we wish to acknowledge generous support from the Queensland Premier's Department, the US Office of Naval Research and from our corporate sponsors Pharmacia (Australia) Pty Ltd, Varian (Australia) Pty Ltd, and Beckman Instruments (Australia) Pty Ltd. Analytical Instruments Pty Ltd, Sunstate Airlines, Australian Airlines and QANTAS also provided valuable assistance.

The University of Queensland welcomes you to its Heron Island Research Station (HIRS) and hopes that you have a professionally rewarding and socially enjoyable stay at the Station. Professor Jiro Kikkawa is Acting Director of HIRS and the Organizers are very grateful that Professor Kikkawa is able to be with us throughout the Workshop.

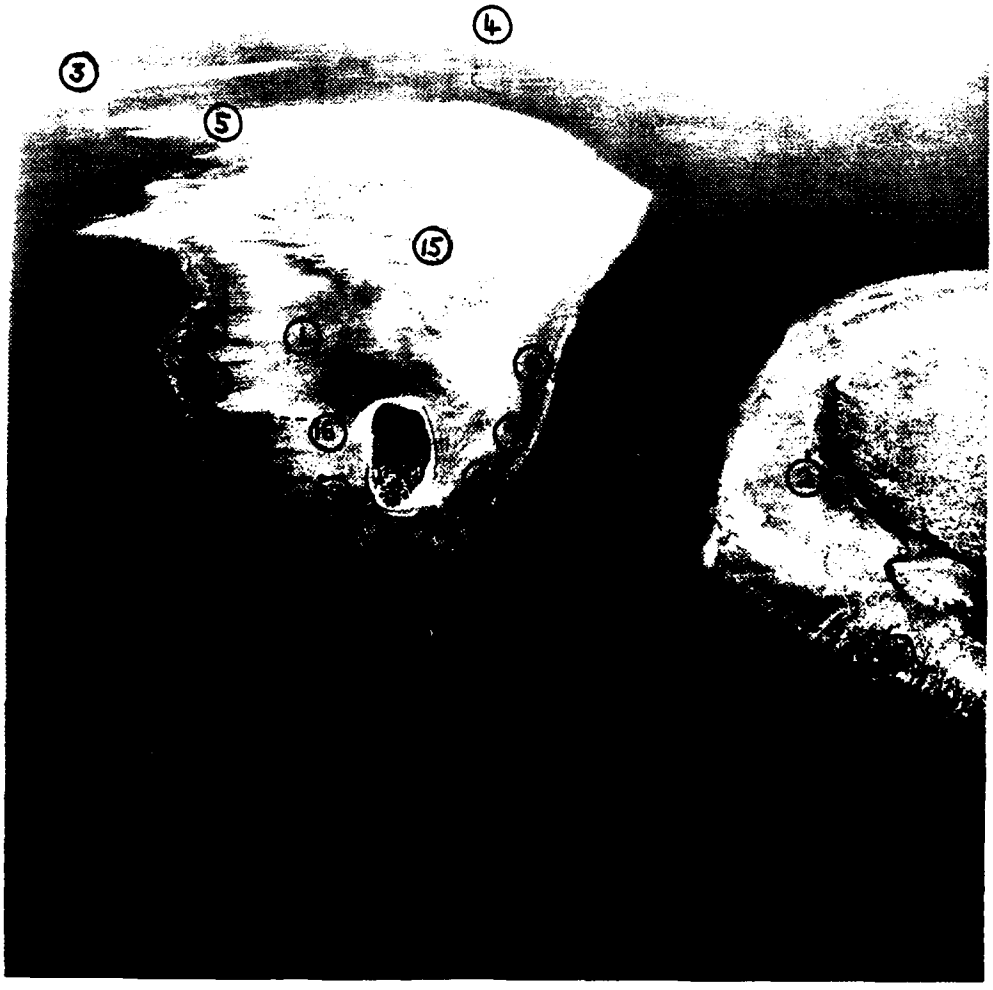
The Heron Island Resort Pty Ltd, (operated by P & O Resorts), has given important assistance to the Workshop. They have made their Pandanus Lounge available for the seminar program and have provided a great environment in which to relax after our hard day's work.

If we can be of help, please approach one of the Organizers or their assistants. We would be delighted to assist you.

Margo Balfour
Cliff Hawkins
Ken Raymond

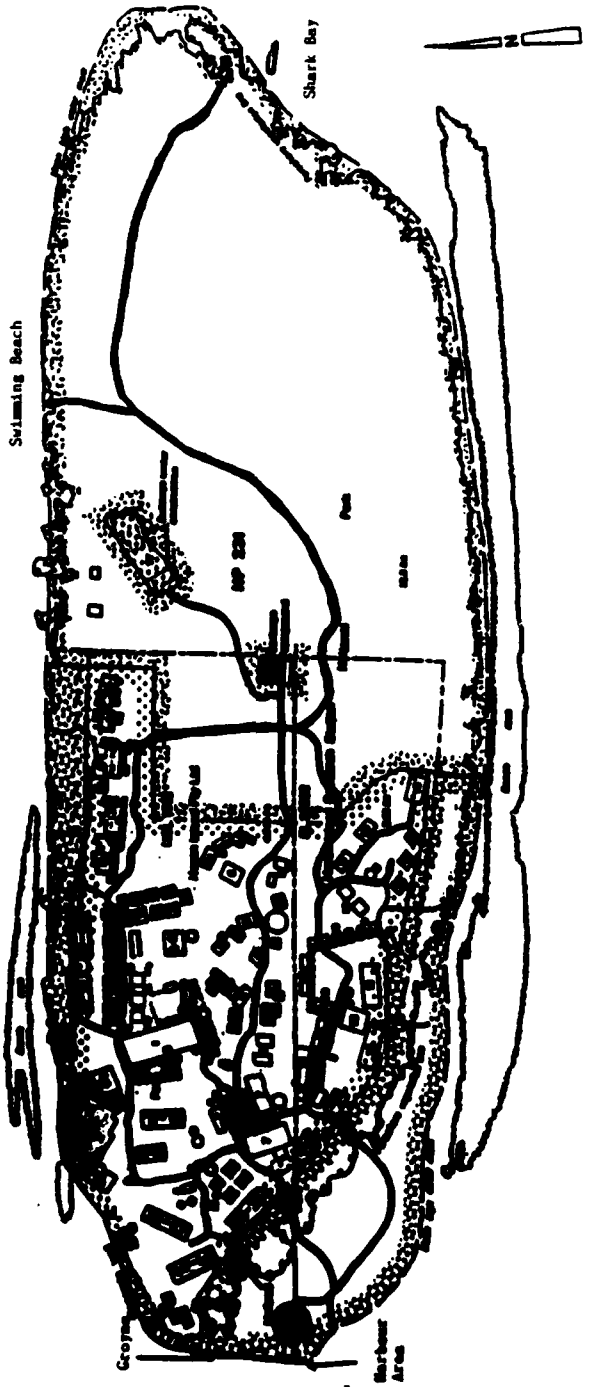
4.

HERON REEF



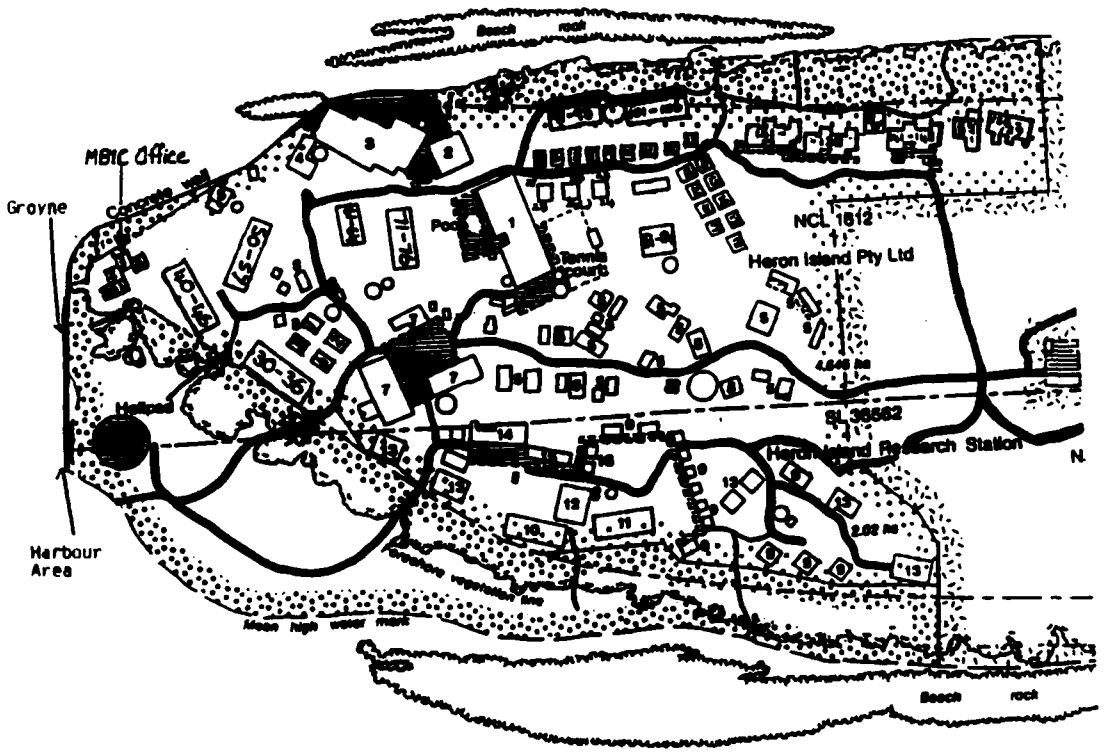
Site References:

1. Heron Reef
2. Wistari Reef
3. Sykes Reef
4. One Tree Island
5. North East Reef Crest
6. North Reef Crest-Zone A
7. South Reef Crest-Zone B
8. Blue Pools
9. The Canyons-Zone C
10. The Bommie
11. Pam's Point
12. The Tenements
13. The Coral Gardens
14. The Gorgonean Hole
15. Lagoon
16. North Reef Collection Walk
17. General Reef Walk Zone
18. Wistari North Crest-Zone D


Shark Bay
Swimming Beach

6.

RESEARCH STATION AND RESORT



Resort:

1. Dining Room & Kitchen
2. Shop and Dive Store
203. MBIC Office
3. Entertainment Complex
4. Offices
5. Staff Accommodation
6. Guest Accommodation
7. Garage/Laundry/Generator/ Workshop/Store
8. Toilets

Station:

9. Visitors Accommodation
10. Offices/Laboratory
11. Laboratory/Library/Museum
12. Aquarium
13. Staff Accommodation
14. Boat Shed
15. Kitchen and Dining Room
16. Toilets

STAFF:

Acting Director:	Prof. Jiro Kikkawa	Clerical Asst.:	Elana Anastase
Director:	Ian Lawn	Boatsman:	Frank Stork
Secretary:	Irene Hall	Maintenance:	Gordon Paul
Research Assist:	Andrew Flower	Blds. & Grds:	David Anastase
Maint. Tech.	Wayne Morrison	Cleaner:	Shirley Paul
Lab. Attendant:	Marlou Stork	Cleaner:	Kay Morrison

Address:	Heron Island Research Station		
	Heron Island		
	Via Gladstone	Phone:	61-79-781399
	Queensland Australia 4680	Fax:	61-79-781457

MEALS: To reduce the cost of accomodation at HIRS the preparation of meals is being done by "volunteers" under the control of Sue Hawkins, who has an Associate Diploma in Catering and Hospitality. Other "volunteers" include Bernice Hawkins, Kate Hawkins, Barbara Raymond and Lisl Swinehart.

All meals for people with HIRS accommodation will be served in the large dining room at HIRS. Meals cannot be taken at the Resort unless you are staying there. The reverse also applies: people with accommodation at the Resort should eat at the Resort and not at HIRS.

	(Island Time)
BREAKFAST HIRS:	0700-0900
LUNCH HIRS:	1130-1400
DINNER HIRS:	1800-2000

Limited wine, beer and orange juice will be available with the evening meal (included in the price). The bars at the Resort will be open to Workshop participants at other times.

WATER: There are two types of water. The normal taps have reverse-osmosis quality water and is fine for drinking. **It is particularly important to conserve this water** as we have a quota that we buy from the Resort. There are special salt water taps for aquaria and for washing the sand off feet, etc.

LAUNDRY: A laundry is available in the ablutions block, but you are asked to keep the use of these facilities to a minimum to conserve water and power.

DIVE LOCKERS: Lockers and hangers for diving gear are available in the ablutions block. Keys can be obtained via David Parry.

DIVERS:

1) All divers must register at the office. Bring "C-card" and medical certificate (you cannot dive without them).
2) Diving is under the direction of Frank Stork.
3) All diving must be done in pairs. Divers with less than 20 hours of logged dives must be accompanied by experienced dive buddies.
4) There will be no night dives.
5) Divers who fail to comply with HIRS diving regulations may be denied access to the Station's facilities.

HERON ISLAND RESORT

MANAGERS:	Michael and Heather Steiner
Address:	Heron Island Resort Pty Ltd
	Heron Island
	Via Gladstone
	Queensland Australia 4680
Phone:	61-79-781488
Fax:	61-79-781457
Telex:	49455

MEALS:
Delegates accommodated at the Resort will eat at the Resort. You may arrive for your meal at anytime within the times:

	(Island Time)
BREAKFAST:	0745-0845
LUNCH:	1230-1330
DINNER:	1830-1930

OFFICE HOURS: 0845-1800
Emergency number after hours dial 33 (internal phone). For settling accounts other than accommodation and for postage stamps, extra laundry, security lock-up and general activities.

MBIC OFFICE HOURS AT THE POINT SUITE 203:
1600-1800 WEDNESDAY; 0700-0745 THURSDAY, FRIDAY & SATURDAY
For accommodation and travel information contact Margo Balfour at the 203 Point Suite, or Cliff Hawkins at HIRS. All outstanding registration/accommodation matters and payments, and grant payments are to be settled as soon as possible after arrival. Additional MBIC sweatshirts at $20 each can be purchased.

SHOP HOURS: 0815-1900
For purchases and activities bookings.

CLINIC HOURS: 1700-1730
The clinic which is at the rear of the Resort Office, is for minor injuries and illness. For emergencies contact the office. After 1700 contact the bar.

BAR HOURS: 1000-2400 TURTLE BAR/PANDANUS LOUNGE

FIRST AID:
Use a sunscreen, wear a hat and avoid coral cuts. If you are cut see an Organizer as soon as possible to have the cut treated with gentian violet.

WORKSHOP PROGRAM

(Note all times are Island Time = Mainland Time + 1 hour)

Wednesday 28 June

1130-1400	HIRS - Lunch	**Pay any outstanding registration and accommodation to MBIC Office on arrival.**
1230-1330	Resort - Lunch	
1400-1800	Activities	
1800-2000	Dinner	
2000-2200	Seminar W1 - Pandanus Lounge	
2200-2400	Music for dancing - Pandanus Lounge	

Thursday 29 June

0700-0900	HIRS - Breakfast
0745-0845	Resort - Breakfast
0900-1230	Field Work
1130-1400	HIRS - Lunch
1230-1330	Resort - Lunch
1330-1600	Field Work/Laboratory Work
1600-1800	Seminar T1 - Pandanus Lounge
1800-2000	Dinner
2000-2200	Seminar T2 - Pandanus Lounge
2200-2400	Music for dancing - Pandanus Lounge

Friday 30 June

0700-0900	HIRS Breakfast
0745-0845	Resort Breakfast
0900-1300	Field Work/Laboratory Work
1130-1400	HIRS Lunch
1230-1330	Resort Lunch
1330-1600	Field Work/Laboratory Work
1600-1800	Seminar F1 - Pandanus Lounge
1800-2000	HIRS Dinner
2000-2200	Seminar F2 - Pandanus Lounge
2200-2400	Music for dancing - Pandanus Lounge

Saturday 1 July

0700-0900	HIRS Breakfast	**Check departure arrangements; pay accounts for drinks and activities, etc. at Reception. After accounts have been paid, all further purchases will be by cash only.**
0745-0845	Resort Breakfast	
0900-1330	Field Work/Laboratory Work	
1130-1400	HIRS Lunch	
0745-0845	Resort Lunch	
1330-1600	Field Work/Laboratory Work	
1600-1800	Seminar S1 - Pandanus Lounge	
1800-2000	Dinner	
2000-2100	Seminar S2 - Pandanus Lounge	
2100-2400	Closing social - Pandanus Lounge	

Sunday 2 July

0500-0600	Snack for people on early catamaran
0600	First catamaran boarding time
0630	First catamaran departure
0700-0900	HIRS Breakfast
0745-0845	Resort Breakfast
0900-1130	Packing for departure
1130	Second catamaran boarding time
1200	Second catamaran departure

WORKSHOP PROGRAM

FIELD WORK:

Manager:	David Parry
Assistants:	Geoff Nette, Steven Taylor, Stephen Brand, Anna van den Brenk, Therese Donlevy, Ken Zimmerman, David Brunckhorst, Alison Green, Andrew Flowers.
Boatsman & Dive Officer:	Frank Stork
Reference:	Australian Coral Reef Handbook

IMPORTANT:

a) Collection Permits: See David Parry

b) Export Permits: See David Parry; Instructions on Page W4.

c) Various field work exercises must be booked during the evening session prior to the exercise. Booking sheets will be on the Workshop's notice Board.

d) *Tide Times: You should note the tide times before you venture out onto the Reef:*

Wednesday	28 June:	1024, 0.73m;	1637, 2.58m
Thursday	29 June:	1123, 0.66m;	1758, 2.77m
Friday	30 June:	1220, 0.60m;	1854, 2.91m
Saturday	1 July:	0707, 2.15m;	1312, 0.56m

REEF WALKS: (Dive shoes, or sports shoes preferably with sox are essential).
Meeting Point: Outside the dining room.

Times:	Thursday	1000-1230 (approx.)
	Friday	1030-1330 (approx.)
	Saturday	1100-1330 (approx.)

a) Collection: Delegates must have equipment ready ahead of time. Guides will lead collectors to areas where organisms are known to exist.
b) Observation: Guides will lead small parties on planned walks to the reef crest to show examples of reef organisms.

ISLAND WALKS: (Thongs, sandals or sports shoes recommended). Professor Jiro Kikkawa (a distinguished ornithologist) and Bernice Hawkins will lead groups on a circuit of the Pisonia Forest in the National Park to identify various plants and birds that exist on the Island.

Meeting Point:	HIRS Seminar Room
Times:	Each day at 1330-1530

SNORKELLING/SCUBA: If weather permits, a group will be taken to various dive sites each morning and afternoon. Collections must be pre-arranged with David Parry. Tanks and weights must also be booked the evening before with David.

Meeting Point:	Boat Shed
Times:	Each day at 0830-1200; 1330-1530

NINE BASIC SAFETY RULES FOR THE REEF:

Field trips can be quite free of even minor injury or accident if basic safety precautions are observed. This set of rules ensures that everyone can enjoy the whole field trip without mishap.

i) Never wander over the reef or island by yourself. A "buddy-system" operates on land as well as in the water.

ii) Always wear sandshoes or other protective footwear when reef-walking. Avoid going barefoot on land, too.

iii) Use gloves if you have to handle an animal unless you definitely know it's harmless. Learn to recognise toxic and venomous reef-top animals and don't touch these at all. Don't rub your eyes with your hands after touching marine life.

iv) Don't harass animals. Defensive mechanisms are likely to operate if creatures are disturbed (eg A ray will normally move quietly away or remain stationary if it detects your presence, but if cornered it will defend itself).

v) Don't swim in the sea at night.

vi) Be careful of currents when swimming or snorkelling. Swim into the current. Don't swim where currents are strong.

vii) Act cautiously in small boats and observe all necessary safety precautions.

viii) Inform a responsible person in the event of **any** injury. Make sure all coral cuts and scratches are cleaned-up and treated promptly.

ix) Sunburn/heat exhaustion is a health hazzard. "**SLIP** on a shirt; **SLOP** on some cream; **SLAP** on a hat. Make sure you drink extra water before any reef activities.

LABORATORY WORK:

Manager:		Bruce Wild
Assistants:		Dianne Watters, Graeme Hanson
Technical Help:	Pharmacia:	Sally Mack, Jennifer Goss
	Varian:	Annabelle Mitchell, Ray Drysdale, Allan Marks, Brian Diver
	Beckman:	Derek Brown

Bench space will be allocated by Bruce Wild. Chemicals, glassware etc should be taken from the store and a record kept of how much is used. Glassware should be thoroughly cleaned before being returned to the store. Our aim is to assist you so that your experiments can be successfully completed in the rather short period of time that is available.

SEMINARS:

Seminar sessions have been planned for 1600-1800 and 2000-2200 each day except on Saturday when there will be an early close at 2100. They will be held in the Pandanus Lounge in the Resort. The bar will remain open during the seminars but it would of course be appreciated if noise and distractions are kept to a minimum.

Some people not included in the formal program would like to report on their work during the Workshop. Watch the notice board for these talks that will take place in the HIRS Seminar Room.

POST-SEMINAR ENTERTAINMENT:

Music will be played in the Pandanus Lounge after the close of the seminars and the dance floor will be at your disposal ur 'l midnight. A special function will be held on the Saturday evening.

W4.

EXPORT PERMITS

Conditions of Authorities Held By Registered Scientific Institutions Under The Wildlife Protection (Regulation of Exports and Imports) Act

An Authority held by a Registered Scientific Institution under the Act, allows for the routine export and import of wildlife (*other than live animals*) for the purposes of non-commercial loans, donations or exchanges between registered scientific institutions i.e. Facilitated Exchange.

Exports
As the holder of an Authority, it is not necessary to apply for a permit for each proposed export transaction provided that attached to the package containing the specimens there is an ANPWS label issued in conjunction with the Authority. There are two types of labels issued for facilitated exchange.

(a) MC-type labels are to be used where the specimens are of species from Australia or overseas listed on Schedules 1, 2 or 3 to the Act.
(b) MN-type labels are to be used only for Australian native specimens not listed on Schedules 1, 2 or 3.

The organisation's address and registered code number will be preprinted on each label. The following additional details must be provided on each label used:

(a) A description of the specimens including the scientific name, number/quantity of each species, nature of specimen e.g. blood, skeleton, flowers, cuttings, etc;
(b) the name, address and code number of the receiving institution;
(c) the signature of the officer of the institution who is responsible for authorising the despatch of the specimens.

A *record* of the above information, *including* the label number, must be kept by the organisation and be made available for review by this Service when requested.

Overseas registered scientific institutions whose code numbers end in 'A' are not permitted under the Act to be involved in exchange of specimens listed on the Appendices to the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) or on Schedules 1, 2 or 3 of the Act. Schedule 3 lists all cetaceans and Schedules 1 and 2 (copy available for perusal) comprise the following categories:

Schedule 1:

* Appendix 1 to the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) - except cetaceans;
* the offical list of Australian endangered vertebrate fauna endorsed by the Council of Nature Conservation Ministers (CONCOM);
* rare birds listed in the Agreement between the Government of Australia and the Government of Japan for the Protection of Migratory Birds and Birds in Danger of Extinction and their Environment.

Schedule 2:

* Appendix II to CITES - except cetaceans.

PARTICIPANT WORK SUMMARY

The Organizers are required, as a condition by the Granting and Permit-Issuing bodies, to prepare reports on the Workshop. Workshop delegates who participate in experiments should submit to Professor Hawkins a handwritten report by **SATURDAY EVENING 1 JULY**. A photocopy will be returned to you for reference, time permitting. A more detailed typewritten report should be submitted with any attachments by **1 AUGUST 1989.**

Name:.....

Institution:.....

Major equipment used (Give brand name):.....

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Assessment of equipment performance:.....

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Organisms collected and quantity:.....

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Organisms & quantity for export (See pages W2 and W4 for procedures):.....

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Experiments, results, comments (Use additional pages if necessary):.....

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W6.

PARTICIPANT COMMENT PAGE

The Organizers would welcome comments on all aspects of the Workshop. These will assist in the evaluation of the Workshop and in the preparation of Reports. Please hand comment sheets to Professor Hawkins by **SATURDAY EVENING 1 JULY.** A photocopy will be returned to you for reference, time permitting.

Name:.....

Institution:.....

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Comments:.....

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SEMINAR PROGRAM

WEDNESDAY 28 JUNE:

2000-2200	**Seminar W1:**	**The Ocean and Seas**
	Cliff Hawkins	Welcome and Workshop Overview
	Francois Morel	Trace Metals & Phytoplankton in the Sea
	Alan Bond	Metals, Quantification & Speciation
	Rita Colwell	Marine Microorganisms

THURSDAY 29 JUNE:

1600-1800	**Seminar T1:**	**Arsenic Chemistry of Marine Organisms**
	Kevin Francesconi	Arsenic in the Marine Environment
	Bill Cullen	Arsenic Marine Chemistry
	Norman Chasteen	Biomineralization in Marine Organisms
	John Webb	Marine Ferritins & Other Iron Materials
2000-2200	**Seminars T2:**	**Marine Algae**
	Alison Butler	Review of Haloperoxidases
	Ron Wever	Vanadium Haloperoxidases
	Hans Vilter	Vanadium Haloperoxidases
	Peter Ford	Marine Photosynthesis
	Vincent Pecoraro	Manganese Chemistry

FRIDAY 30 JUNE:

1600-1800	**Seminars F1:**	**The Ascidians**
	Ken Kustin	Metal Chemistry of Ascidians
	Jim Swinehart	Uptake of Metals by Ascidians
	Cliff Hawkins	Vanadium and Iron Proteins
	Herbert Waite	Metal Complexing of Adhesive Protein
2000-2200	**Seminars F2:**	**Marine Iron Proteins**
	Stephen Lippard	A Review
	Karl Wieghardt	Model Systems
	Keith Murray	Model Systems
	David Dolphin	P-450 & Heme Peroxidases

SATURDAY 1 JULY:

1600-1800	**Seminars S1:**	**Copper, and Molybdenum Systems**
	Tony Wedd	Marine Molybdenum Proteins
	Hans Freeman	Copper Proteins: Introduction
	Geoff Sykes	Hemocyanin
	Tom Sorrell	Models for Hemocyanin
2000-2100	**Seminars S2:**	**Summary and the Future**
	Alan Sargeson	Speakers will report on their work and
	Dick Holm	will comments on the various papers,
	Ken Raymond	and look to the future.
	Cliff Hawkins	Closure

TRACE METALS AND PHYTOPLANKTON IN THE SEA

F.M.M. Morel

Ralph M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

Over the last decade, extreme attention to contamination problems has allowed oceanographers to determine the concentration of trace metals in seawater. Many trace elements including Mn, Ni, Co, Fe, Zn, Cd, and Cu are at nanomolar and lower concentrations in the surface ocean. These concentrations exhibit characteristic profiles that increase with depth and suggest removal by the biota in the photic zone. Since they behave geochemically like phosphorus and nitrogen, one may wonder if trace metals also act as "limiting" nutrients. Some of the critical requirements for these elements have been shown in laboratory experiments and their uptake kinetics are being elucidated.

METALS, QUANTIFICATION AND SPECIATION

A.M. Bond

Department of Chemical and Analytical Sciences, Deakin University, Geelong, Victoria 3217, Australia.

Many metals of interest in seawater exist at concentrations well below the 1 part per billion level. Over the last twenty or more years, substantial effort has been made at reliably determining the concentrations of such metals. Errors have been frequent but some progress is now being made towards obtaining reliable data. An even more severe challenge now facing us is to actually identify the chemical form (speciation) of the metals present. If the total concentration is less than 1 part per billion, then this is an extremely demanding and difficult task. There are relatively few techniques available for metal determination in seawater that are applicable at the parts per trillion level. Even fewer can undertake speciation investigations at this concentration level. One approach is of course to concentrate the metal by solvent extraction or other means. However, any work requiring the addition of chemical reagents to seawater runs the risk of modifying the sample being investigated. It is also a very challenging task to successfully transfer a sample from the ocean to a laboratory and not modify it via contamination, change in dissolved CO_2 (pH) etc. The alternative to taking the sample to the laboratory for analysis is to take the equipment to the sea and undertake examination of metal concentrations directly using battery powered scientific instrumentation. In this talk, a review of electrochemical techniques that can be applied to the determination and speciation of low concentrations of metals in seawater will be presented. In particular the merits and problems of transporting samples to the laboratory versus direct examination in the sea will be considered. Possibilities for speciation studies without chemical manipulation of samples will be emphasised. Limitations with existing methods will be discussed, as will possiblities in the future with computer based battery operated instrumentation.

A2.

ABSTRACTS-W1

MARINE MICROORGANISMS

R.R. Colwell

Maryland Biotechnology Institute and Department of Microbiology, University of Maryland, College Park, Maryland 20742, USA.

Heterotrophic bacterial populations have been isolated from marine invertebrates, including reef sponges. The classes of heterotrophic bacterial associations include: populations of cosmopolitan bacteria of a species composition similar to that of ambient sea water, in which case the bacteria will very likely provide a food source; specific populations inhabiting the invertebrate fauna and representing microorganisms not found in the ambient sea water, e.g., candidate symbionts and bacteria of very small size located intracellularly (Santavy and Colwell, 1989). Complex bacterial communities have been shown to be associated with the Bahamian sclerosponge *Ceratoporella nicholsoni*, providing an interesting model of symbiosis.

Culturable sponge symbionts were found to represent two new species of marine *Vibrio*, a new species of marine *Aeromonas* and other, as yet to be identified, microorganisms. The symbionts include marine bacteria with an obligate requirement for NaCl and the ability to degrade a large number of complex molecules. The bacterial community composition associated with *Ceratoporella nicholsoni* was found to be different from those previously reported for other Porifera. In fact, a "universal symbiont" phenotype does not exist, since the phenotype associated with other sponges from different locations was not present in the Bahamian sponges.

Interactions of *Vibrio* species with invertebrate animals has proven interesting, and recent findings indicate production of neurotransmitter compounds by marine *Vibrio* sp., which function to attract larvae of invertebrates to settlement. Also, these compounds appear to play a role in metamorphosis. Studies of an *Alteromonas* sp. associated with the Chesapeake Bay oyster *Crassostrea virginica* has shown it to demonstrate specific interactions mediated by its metabolites.

Recent documentation of production of tetrodotoxin by marine bacteria, including marine *Vibrio* spp., including *V.cholerae*, strongly suggests that toxins are produced by microbial symbionts of the host animal. Symbionts related to the Vibrionaceae, Aeromonadaceae, and Enterobacteriaceae have been found to be associated with production of bioactive metabolites, since these organisms are adept in exploiting nutrient-rich environments. The Pseudomonadaceae, however, appear to be better adapted to survival in oligotrophic waters, such as those found in overlying coral reefs.

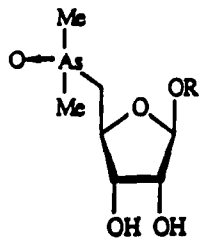
THE TRANSFORMATION OF ARSENIC IN THE MARINE ENVIRONMENT

K.A. Francesconi and J.S. Edmonds

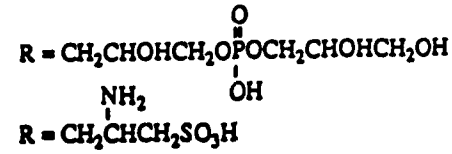
Western Australian Marine Research Laboratories, PO Box 20, North Beach, W.A., 6020, Australia.

It has been known since the 1920s that marine organisms contain high levels of arsenic, generally in the range of 1-40μg/g wet weight. In 1977 the arsenic constituent of the western rock lobster, *Panulirus cygnus*, was shown to be trimethylarsoniumbetaine (arsenobetaine, $Me_3As^+CH_2COO^-$) [1] and subsequent work has established that arsenobetaine is the sole or major form of arsenic in a wide range of marine animals [2]. Evidence suggests that arsenobetaine is accumulated by marine animals *via* the food chain rather than directly from seawater. Arsenic occurs in seawater at ~2μg/L and exists largely as arsenate with smaller quantities of arsenite and the simple mono and dimethylated arsenic acids.

The levels of arsenic in marine macroalgae are comparable to those found in marine animals. Examination of the form of arsenic in several species of brown algae has shown that dimethylarsinylribosides occur as major constituents [3]. Arsenate occurs in varying amounts and a trimethylarsoniumriboside has been found in one species of brown alga in trace amounts. Arsenobetaine is not present. Radiolabelling studies using ^{74}As arsenate in seawater have demonstrated that unicellular algae rapidly transform the arsenate into dimethylarsinylribosides. The biosynthesis of these algal arsenic compounds may involve sequential reduction and methylation of arsenate by S-adenosylmethionine. Further, dimethylarsinylribosides present in marine algae may serve as precursors to arsenobetaine found in marine animals. The biosynthesis of dimethylarsinylribosides and their possible conversion to arsenobetaine in biological systems are currently under study.



R = $CH_2CHOHCH_2OH$
R = $CH_2CHOHCH_2SO_3H$
R = $CH_2CHOHCH_2OSO_3H$



DIMETHYLARSINYLRIBOSIDES

1. Edmonds,J.S., Francesconi,K.A., Cannon,J.R., Raston,C.L., Skelton,B.W. and White,A.H., *Tetrahedron Lett*, 1977, 1543.
2. GESAMP, Rep. Stud. GESAMP, **28**, 1987.
3. Edmonds,J.S. and Francesconi,K.A., *Experientia*, 1987, **43**, 553.

ARSENIC AND TIN SPECIATION IN THE MARINE FAUNA OF BRITISH COLUMBIA

W.R. Cullen

Department of Chemistry, University of British Columbia, Vancouver, B.C., V67 1Y6, Canada.

The water-soluble arsenic compounds in five species of clams--Butter clam (*Saxidomus giganteus*), Horse clam (*Schizothoerus nuttalli*), Soft-shelled clam (*Mya arenaria*), Native littleneck clam (*Protothaca staminea*), and Manila clam (*Venerupis japonica*)--are described. Varying amounts of arsenobetaine and tetramethylarsonium ion are the major arsenicals found in all species. Butter clams show the presence of a third compound that appears to be trimethylarsine oxide. Gastropods have high concentrations of these and other arsenicals. Organotin compounds, mainly butyl derivatives, are also present in these animals. Their shells contain inorganic arsenic and antimony, methylarsenicals, and butyltin compounds.

BIOMINERALIZATION IN MARINE ORGANISMS

N.D. Chasteen

Department of Chemistry, University of New Hampshire, Durham, N.H. 03824, USA.

The calcareous exoskeletons of marine organisms vary widely in form and detailed composition. The shells of most bivalve mollusks are composed of calcite and/or aragonite in a highly ordered microstructure in intimate association with an organic matrix. The shell is normally covered by an outer layer of quinone tanned protein called the periostracum. Components of the shell are secreted by the mantle, a biochemically active organ which is composed of two epithelial cell layers that separate the soft parts of the animal from the shell. Sandwiched between the mantle and the developing shell is the extrapallial fluid, a complex mixture of mucopolysaccharides, glycoproteins, amino acids, peptides, organic acids and inorganic ions. It is within this fluid that the complex chemistry of shell formation takes place.

This lecture will present an overview of calcification in bivalve mollusks with emphasis on studies conducted in the author's laboratory. Topics to be discussed include the chemical and spectral characterization of the extrapallial fluid of the blue mussel *Mytilus edulis* and the role of the EP fluid in calcification. The use of 'single crystal' EPR spectroscopy of naturally occuring Mn(II) ions as a probe of the microstructure of the calcarious shells of the blue mussel, the soft shelled clam (*Mya arenaria*), and the common barnacle (*Balanus balanoides*) will also be discussed.

MARINE FERRITINS AND OTHER IRON MATERIALS

J. Webb, T.G. St. Pierre and D.J. Macey*

School of Mathematical and Physical Sciences, and *School of Biological and Environmental Sciences, Murdoch University, Murdoch, Perth, W.A., 6150, Australia.

The iron-binding protein ferritin is constructed, in general, of an array of polypeptide chains organized into a roughly spherical shell within which can be found an iron-containing particulate phase, the so-called "iron core", that can be readily visualized under the electron microscope. Such a structural motif has now been observed for ferritins from a wide variety of living organisms, including bacteria, plants, invertebrates and vertebrates.

Marine ferritins have been isolated recently from the hemolymph (blood) of molluscs such as chitons and limpets that incorporate iron minerals into composite materials that make up the hard structural components of the teeth on their radula (tongue). The radulas are used to scrape algae from rocks in near and intertidal regions and, in the process, are continuously worn away thus necessitating the continual production of more iron minerals to replace those lost with the discarded teeth. This high turnover of iron may be related to the exceptionally high concentration of ferritin found in the hemolymph, where ferritin provides a high capacity transport system necessary to deliver iron to the rapidly and continually mineralizing radula tissue.

The iron cores of these marine ferritins differ from that of mammalian ferritin in that they are of larger volume, contain less Fe atoms and fewer phosphate groups and are of lower crystallinity in their ferrihydrite-like phase ($5Fe_2O_3{\cdot}9H_2O$). They differ also in their magnetic properties as shown by the temperature dependence of their Mössbauer spectra.

The paper will highlight the structural similarities and differences among the mineral phases of the cores of these functionally-related ferritins. This information is pertinent, since any difference in core structure must be derived from mechanistic factors of mineral formation that may ultimately be related to functional adaption. For example, structural and compositional parameters will have a marked influence on the rates of iron storage and mobilization by the ferritin molecule and hence on its role in iron homeostasis, storage and transport. The other iron materials found in marine systems, particularly the chitons and limpets (magnetite Fe_3O_4; goethite μ-FeOOH; lepidocrocite γ-FeOOH; hydrous iron(III) phosphate), will also be considered.

THE NOVEL, NON-HEME VANADIUM AND IRON BROMOPEROXIDASES FROM MARINE ALGAE: KINETIC AND MECHANISTIC INVESTIGATIONS OF THE NATIVE AND METAL EXCHANGED DERIVATIVES

A. Butler, R.R. Everett, R.T. Reid, H.S. Soedjak

Department of Chemistry, University of California, Santa Barbara, CA 93106, USA.

Vanadium-bromoperoxidase (V-BrPO) and non-heme iron bromoperoxidase (Fe_{NH}-BrPO) are recently discovered metalloenzymes in marine algae. Both V-BrPO and Fe_{NH}-BrPO catalyze the oxidation of bromide by hydrogen peroxide which results in the bromination of many organic substrates or the halide-assisted disproportionation of hydrogen peroxide, forming singlet dioxygen, in the absence of a suitable organic substrate for bromination. The yield and rate of singlet oxygen production has been measured by direct observation of the 1268nm chemiluminescence. In contrast to FeHeme haloperoxidases, neither V-BrPO and Fe_{NH}-BrPO catalyze the direct disproportionation of H_2O_2. Both V-BrPO and Fe_{NH}-BrPO are remarkably similar in many physical characteristics, (e.g., subunit molecular weight, amino acid composition, isoelectric point, etc) and in the nature of the catalytic chemistry, suggesting that iron and vanadium may be exchanged, producing active derivatives. Indeed, vanadium (V) can be substituted for iron in Fe_{NH}-BrPO, producing an active derivative (i.e., V'-BrPO) with identical mechanistic characteristics to the native Fe_{NH}-BrPO.

STRUCTURE AND FUNCTION OF VANADIUM BROMOPEROXIDASES

R. Wever, B.E. Krenn, M.G.M. Tromp and H. Plat

Lab. of Biochemistry and Biotechnological Centre, University of Amsterdam, PO Box 20151, 1000 HD Amsterdam, The Netherlands.

Organisms such as algae, lichens, fungi and bacteria contribute large quantities of organohalo species to our ecosystem. In particular brown seaweeds produce high amounts of rather simple volatile brominated compounds like CH_2Br_2 and $CHBr_3$. This is of considerable interest since there may be a link between the periodic ozone destruction observed in the Arctic atmosphere and bromoform produced biologically. Vanadium bromoperoxidases from seaweeds appear to be involved since they are present in these seaweeds and are able to oxidize Br^- with H_2O_2 to HOBr and Br_2.

These enzymes rapidly loose their activity at low pH and in this way an apo-enzyme can be prepared. Reconstitution of the activity occurs when vanadate (VO_4^{3-}) is added. From titration data of the apo-enzyme with vanadate it was possible to evaluate the binding constant (K_d = 36 nM) for this reaction. Upon reduction of bromoperoxidases from various species of seaweed and a lichen, essentially the same type of EPR spectrum is observed. The spectral parameters (Table 1) suggest that the structure of the active sites in the enzymes is very similar.

STRUCTURE AND FUNCTION OF VANADIUM BROMOPEROXIDASES (Continued)

Table 1 EPR data of reduced bromoperoxidase

species	$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$ (mT)	$A_{\parallel}$ (mT)
L. saccharina	1.979	1.948	5.7	17.6
A. nodosum	1.979	1.948	5.5	17.6
X. parietina	1.979	1.945	5.8	17.7
C. pilulifera	1.974	1.946	5.8	17.8

EXAFS studies on native bromoperoxidase from *Ascophyllum nodosum* show that the data for the active site can be described by vanadium V ligated to one oxygen at 1.61 , three oxygens at 1.72 and two nitrogens at 2.11 . These short oxygen distances are typical of vanadate and vanadium (V)-alkoxy systems. Steady-state kinetics of the bromination reaction correspond to a mechanism in which H_2O_2 first has to modify a site on the enzyme before bromide can be bound. We suggest that the vanadium ion in bromoperoxidases serves as a binding site for H_2O_2. Probably hypobromite is formed when the bromide ion is oxidized by the peroxo-vanadate intermediate. Despite the presence of the same prosthetic group in these enzymes, (probably with comparable ligand field environments) the enzymic properties are very different.

VANADIUM HALOPEROXIDASES

H. Vilter

Institute for Pharmaceutical Biology, University of Bonn, Nuballee 6, D-5300 Bonn, West Germany.

The first vanadium containing peroxidase (A.n.I) was detected in the brown alga *Ascophyllum nodosum*[1]. The peroxidase does not belong to the hemoproteins as indicated by the lack of the Soeret-band in the electron absorption spectrum [2,3]. During a screening program using material from Europe, Canada, Japan, South Africa and New Zealand further vanadium containing peroxidases were detected in a large number of several brown algae. These algae are belonging predominantly to the Fucaceae and the Laminariales. However vanadium containing peroxidases were not detectable in red algae, green algae, fungi and lichen. The vanadium containing peroxidase catalyzes the oxidation of iodide, bromide and thiocyanide. In contrast to the typical heme-containing peroxidases the vanadium-containing peroxidase is not inhibited by the reaction products. The apoenzyme was prepared by dialysis. Only by adding vanadate to the inactive apoenzyme, the active enzyme was reconstituted. No active derivative was obtained by metal substitution. In the native enzyme the oxidation state (V) of the vanadium was detected by ^{51}V NMR [4,5] and X-ray absorption spectroscopy [6].These spectroscopical studies indicate, that the vanadium(V) is surrounded by six to eight oxygen functions under the participation of carboxylate groups. The binding of the substrates are studied using NMR-techniques.

VANADIUM HALOPEROXIDASES (Continued)

To solve the three-dimensional structure in order to gain detailed insights into the unusual type of peroxidases the vanadium containing A.n.I was crystallized [7]. Several grams of enzyme were needed during the studies. Several hundred kilograms of raw material had to be extracted in a pilot plant. The technological problems due to the high contents of alginates and polyphenols, and the different strategies to solve these problems will be discussed.

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MARINE PHOTOCHEMISTRY-AN INORGANIC CHEMIST'S VIEW

P.C. Ford

Department of Chemistry, University of California, Santa Barbara, CA 93106, USA.

Photochemical processes in marine systems will be discussed with the goal of providing an overall perspective as to what roles light plays in natural waters. Several systems involving inorganic problems of current interest to marine chemistry will be reviewed, and attempts will be made to suggest new directions where laboratory research may provide added insight into such processes.

MANGANESE CHEMISTRY

V. Pecoraro

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan, 48109-1055, USA.

Manganese is an essential component of the photosynthetic water oxidizing system of algae and higher plants. Although four manganese are required for optimal enzymatic activity, little is known about the active site structure (nuclearity and metal orientation) or metal oxidation states accessed during the catalytic cycle. An examination of possible structural organisations for the manganese ions using a dual center model will be presented. In addition, the possible role of calcium and chloride in enzymatic function will be discussed.

VANADIUM CHEMISTRY OF ASCIDIAN BLOOD CELLS

K. Kustin

Department of Chemistry, Brandeis University, Box 9110, Waltham, MA 02254-9110, USA.

Four distinctive features of the blood of many ascidians are predominance of spherical vacuolated cells, pigmentation, appreciable vanadium content, and high *in vitro* acidity of blood cell lysate. What functions do these features of ascidian blood have? Do they serve a common purpose? If they serve a common purpose, why do these features, particularly, pigmentation color and vanadium concentration show such significant interspecies variation? Investigations of ascidian blood chemistry have yielded much interesting information bearing on these questions but few definitive answers. One approach to finding answers confers a central role to vanadium accumulation and relates cell structure, pigmentation, and acidity to the demands vanadium chemistry impose on living cells. This review therefore considers recent experiments on vanadium distribution in ascidian blood cells, blood cell chromophore chemistry, reduction to and stabilization of vanadium(III), and the origin of high acidity in blood cell lysates, and their relation to blood cell morphology and suggested function.

UPTAKE OF METALS BY ASCIDIANS

J.H. Swinehart, D.H. Anderson, and M.A. Caputo

Department of Chemistry, University of California, Davis, CA 95616 USA

Certain ascidians accumulate vanadium to high levels, especially in their blood cells, and it now appears that most, if not all, ascidians accumulate some vanadium. The pathways by which the vanadium(V) in seawater is reduced and enters the blood cells is of interest in understanding where metal selectivity occurs, what factors affect metal selectivity, and, potentially, the role of vanadium in ascidians. Experiments in which the ascidian, *Ascidia ceratodes*, was incubated with the radiotracer V-48 for up to 60 days indicate that a major amount of the vanadium in the blood cells is accumulated in a time period approximating the time required for blood cell development. Only a minor amount of the vanadium incorporated in blood cells is transported rapidly from the seawater to the plasma and into the blood cells. Uptake experiments using phosphate, an inhibitor of vanadium(V) uptake, suggest a different pathway. The significance of these pathways will be discussed. With reference to the problem of metal selectivity, it has been demonstrated from *in vitro* studies that there is selectivity towards vanadium(V) by branchial sacs from ascidians in the order *Styela montereyensis* < *Ciona intestinalis* < *Ascidia ceratodes*. This order parallels the levels to which vanadium is accumulated by the organisms themselves. Experiments have been carried out to determine the differences in the compositions of branchial sac membranes in ascidians that accumulate large to moderate amounts of vanadium (*A. ceratodes, Ascidia callosa, and C. intestinalis*) compared to those that do not (*Pyura haustor, S. montereyensis, and Molgula manhattensis*) in order to ascertain what role differences in composition between species might have on metal uptake. Results from these six ascidians indicate that a major difference occurs in the composition of the nonpolar component of the membranes. The role differences in membrane composition play in metal selectivity will be discussed.

VANADIUM AND IRON PROTEINS IN THE ASCIDIACEA

C.J. Hawkins

Department of Chemistry, University of Queensland, St. Lucia, Queensland 4067, Australia.

The blood of ascidians contains in the cells and in the plasma some unique metalloproteins and small molecular weight chelates. Webb and coworkers isolated a single strand transferrin (40000 da) from the plasma of *Pyura stolonifera*[1]. The cells of this species contain as the predominant protein a DOPA-protein called ferreascidin[2] with a DOPA-oxidase and an inhibitor for the enzyme, homarine (N-methylpicolinate). Ferreascidin (10000 da) has 2 glucose units and a highly aromatic amino acid composition with 42% tyrosine and 17% DOPA[2]. At pH5.9 ferreascidin interacts with $[Fe(NTA)_2]^{3-}$ to form four $[Fe(cat)(NTA)]^{2-}$ units. These are broken down in the presence of homarine. At pH 6.9 two bis(catecholato) iron(III) units are formed. The characterization of these compounds will be described. High concentrations of vanadium are found in the blood cells of aplousobranch and phlebobranch ascidians. Reactions with 2,2-bipyridine and acetylacetone show that the vanadium is predominantly in oxidation state III in the compartment and morula cells. Whole animal esr spectra following oxidation show two modes of coordination corresponding largely to the sub-orders.[3,4] X-ray electron microscopic analysis of the Phlebobranch, *Ascidia julinea*, show that fluorescent material is laid down in distinct bands in the globules. The Aplousobranch, *Leptoclinies lissus*, yields a green vanadium protein. Its properties will be described.

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METAL-COMPLEXING MARINE ADHESIVE PROTEINS

J. Herbert Waite

College of Marine Studies, University of Delaware, Lewes, DE., 19958 USA.

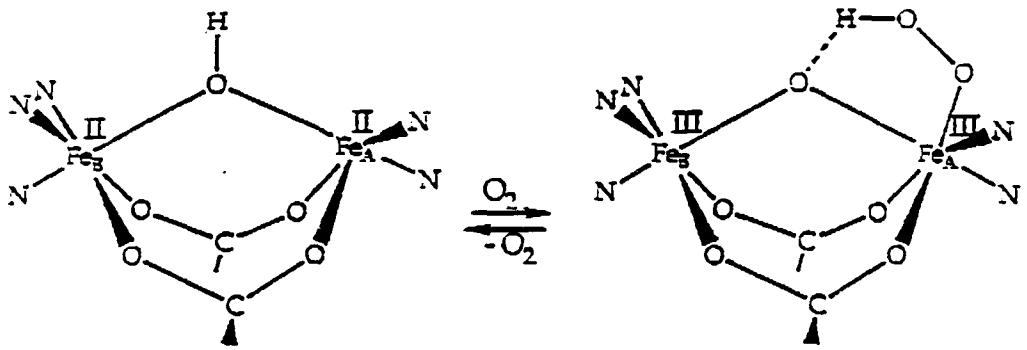
The marine bioadhesives of barnacles, oysters, mussels, reef-building polychaetes, etc., have long intrigued chemical engineers. In recent years, the structure and chemistry of a number of marine adhesive proteins have been elucidated. Although these are very diverse in their primary sequences, they share basic isoelectric points and have high ($>10^{20}$) affinities for a variety of metals including Al, Fe, V, Ti, Zn, Cu etc. This affinity is at least in part due to stable organometallic complexes formed between the metal and 1,2-benzenediol functional groups represented by 3,4-dihydroxyphenyl-L-alanine (DOPA) in the protein. Stable complexes are formed both with metal salts in solution and with insoluble metal oxides. Curiously, despite the large size of some of the adhesives (>100 kD), spectroscopic evidence suggests that they can form mono-, bis-, and tris-complexes with Fe(III), for example. This reflects considerable flexibility in the peptide backbone. Future studies will attempt to characterize the mechanism of metal-binding.

MARINE IRON PROTEINS: REACTIONS OF NONHEME IRON CENTRES WITH DIOXYGEN

S.J. Lippard

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

Hemerythrin (Hr) is the dioxygen transport protein of marine invertebrates from the phyla Sipunculida, Priapulada, and Brachiopoda. The functional core of the deoxy form of the protein consists of an hydroxo-bridged diiron(II) unit that reacts with dioxygen to form oxyHr, as show below:



Deoxyhemerythrin Oxyhemerythrin

The nitrogen atoms in the coordination spheres of iron are contributed from histidine residues of the protein and the carboxylates from aspartate and glutamate residues. The synthesis of several model complexes for the dinuclear cores in deoxy and oxyHr will be reviewed, and tactics for preparing functionally relevant systems will be described.

Another important reaction that can occur in proteins containing a dinuclear iron core is alkane oxidation. Methane monooxygenase (MMO), a mixed function oxidase found in methanotrophs, is one such enzyme. In this chemistry, one atom of dioxygen is tranferred to substrate and the other forms water:

$$CH_4 + O_2 + 2e^- + 2H^+ \rightarrow CH_3OH + H_2O$$

New iron catalysts, derived from $\{Fe_2OCl_6\}^{2-}$ and ascorbic or tetramethylreductic acid, that utilize O_2 to oxidize hydrocarbons at ambient temperature and pressure, will be presented. Factors that contribute to the control of dioxygen reactions at the dinuclear iron centre in a given protein will be discussed. Parallels will be drawn between the use of Hr and MMO to bind or activate dioxygen in primitive organisms and the utilization of heme iron proteins to effect analogous reactions in higher life forms.

ABSTRACTS-F2

MAGNETIC EXCHANGE PATHS IN HETEROBINUCLEAR COMPLEXES CONTAINING AN OXO-BIS(-ACETATO) DIMETAL CORE

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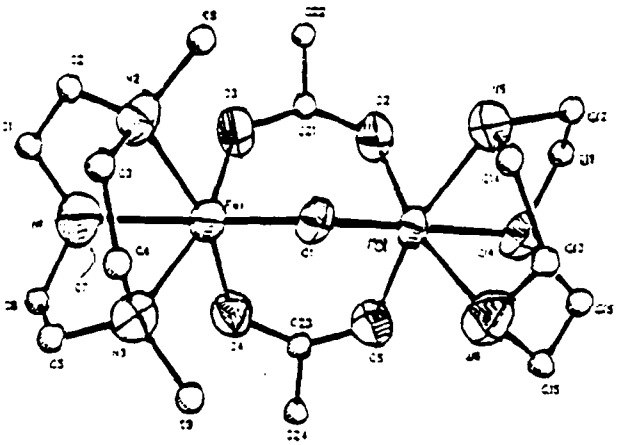
[a] Ruhr-Universitat Bochum, FRG, [b] Universite Paris-Sud, France, [c] Gesamthoschschule Universitat Paderborn, FRG, [d] Victoria University of Wellington, NZ.

Anorganische Chemie I, Ruhr Universitat Bochum, Universitatsstrasse 150, Bochum D-4630, West Germany.

We have synthesized and characterized by X-ray crystallography a series of heterobinuclear complexes containing the μ-oxo-bis(μ-acetato) dimetal core with two different transition metals as well as their homobinuclear counterparts. Hydrolysis of LM^1Cl_3 and $L'M^2Cl_3$ complexes in aqueous solution containing ammonium acetate affords these complexes in good yields. From susceptibility measurements intramolecular ferromagnetic or antiferromagnetic spin exchange coupling has been observed depending solely on the d^n electronic configuration of M^1 and M^2.

M^1	M^2	J,cm^{-1}
Fe(III)	Fe(III)	120
Mn(III)	Mn(III)	+18
Fe(III)	Mn(III)	-145
Fe(III)	Cr(III)	-137
Mn(III)	Cr(III)	+ 2
Cr(III)	V(III)	+18



$H = -2JS_1 \cdot S_2$
L = 1,4,7-triazacyclononane
L' = N,N',N"-trimethyl-1,4,7-triazacyclononane

A detailed analysis of the interacting magnetic orbitals revealed that the d_z^2-d_{xz}-orbital interaction is the dominant magnetic path propagating strong antiferromagnetic exchange coupling when the d_z^2 at one metal site *and* d_{xz}-orbital at the other metal site are occupied by one electron, respectively; depletion of one or both electrons from these orbitals leads to ferromagnetic coupling.

MODEL COMPOUNDS FOR MARINE IRON PROTEINS

K.S. Murray

Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia.

Our experiences in studies of bioinorganic model iron compounds will be discussed in relation to marine iron proteins. Recent studies on mononuclear and polynuclear systems will be described with, in the latter case, emphasis being placed on bridging groups such as Fe-C-Fe, Fe-N-Fe, Fe-(NR)-Fe, Fe-O-Fe, Fe-S-Fe. Structural, magnetic, spectral and redox comparisons of these Fe^{III}- and Fe^{IV}-containing compounds will be made.

CYTOCHROME P-450 AND HEME PEROXIDASES

D. Dolphin

Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, B.C., V6T 1Y6., Canada.

The majority of heme proteins contain iron protoporphyrin as their prosthetic group yet carry out a very diverse range of biochemistry from the transport and storage of dioxygen and electrons, the activation of dioxygen, and the control and utilization of hydrogen peroxide. In fact these reactions have much in common. We plan to show that those enzymes which activate dioxygen (cytochrome P-450) and those that utilize peroxide (particularly the peroxidases) function via a common intermediate and by similar reaction mechanisms. Special emphasis will be placed on the haloperoxidases which along with the non-heme systems account for the large diversity of halogenated chemicals found in the marine environment.

MARINE MOLYBDENUM PROTEINS

A.G. Wedd

Department of Chemistry, La Trobe University, Bundoora, Victoria, 3083, Australia.

While molybdenum is one of the rarer transition elements, it is the most abundant transition element present in sea-water: *ca.* 10 μg dm^{-3}. This follows from the solubility of its available forms, $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$, under the conditions.

The photosynthetic cyanobacteria (blue-green algae) also fix dinitrogen via the molybdo-enzyme nitrogenase. This aspect of marine molybdenum biochemistry is quite well developed. In contrast, the study of oxo-molybdenum enzymes in marine animals, plants and bacteria is undeveloped.

This brief review will outline the present state of play.

COPPER PROTEINS: AN INTRODUCTION

H.C. Freeman

Department of Chemistry, University of Sydney, Sydney, N.S.W. 2006, Australia, 2006.

The final topic for discussion in the Workshop is concerned with copper proteins in marine organisms. Two papers will be presented on the hemocyanins and their models.

The hemocyanins transport oxygen in the hemolymph of many species of invertebrates belonging to the phyla Mollusca and Arthropoda. They are highly aggregated molecules that contain one active site per subunit of molecular weight approximately 50000 (molluscan) to 75000 (arthropodan). The active site of the deoxy protein has two coppers 3.8 $\mp$ 0.4 Å apart with each copper coordinated to three imidazole groups.

REACTIVITY OF HEMOCYANIN AND COMPARISONS WITH HEMERYTHRIN & MYOGLOBIN

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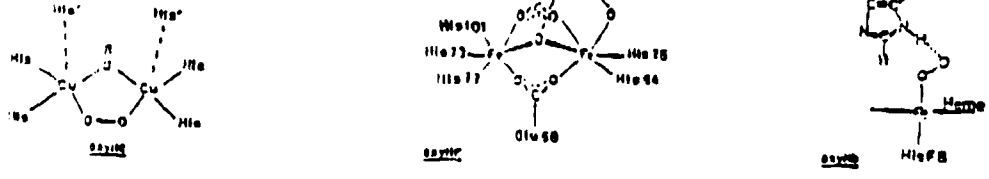
Over 200 oxygenases and oxidases are known in which molecular O_2 is utilised. The three biological O_2-carriers represent relatively simple examples in which binding of O_2 to a metal active site occurs and aspects of recognition can be explored. Deoxy forms are $Cu(I)_2$ for hemocyanin, $Fe(II)_2$ in hemerythrin and heme Fe(II) in myoglobin. Such studies have the advantage of being free from the complications of subsequent steps. Other small molecule redox interconversions are also relevant to a consideration of recognition. Here results have been obtained for hemocyanin and are compared with those for hemerythrin and myoglobin. The emphasis is on molecular recognition and metalloprotein reactivity.

Background: Not only are the active sites of the three O_2 carriers quite different, but the manner in which O_2 is bound is also different. The source of hemocyanin (Hc) was *Panulinus interruptus*; unless otherwise stated the monomer subunit *a* was used. The hemerythrin (Hr) used in our previous studies was *Themiste zostericola* (octamer; M_r 108,000); Hr does not normally exhibit cooperativity. Comparisons are also made with myoglobin (Mb) (M_r 16,000). Active site structures of the oxy forms are shown.



Deoxy with O_2: Data obtained for single-step equilibrations of the three O_2-carriers with O_2, e.g. $Cu(I)_2 + O_2 \rightarrow Cu(II)_2O_2$ will be considered. Results obtained for subunits a, b and c will be reported. Amino-acid sequences for a and b are similar, but there is only 50% homology with c which is of considerable interest.

Deoxy with H_2O_2: Rate constants for the single stage conversion to met forms of Hc and Hr will be discussed.

Interconversion of Deoxy and Met Hc: There is no reaction of the deoxy Hc with $[Fe(CN)_6]^{3-}$ (410 mV). Since there is no reaction either of met Hc with $[Co(sep)]^{2+}$ (-260 mV) as reductant, an explanation in terms of high E^0 for the Hc redox couple is not acceptable, and the difficulty of reducing the buried Hc active site from without is noted. The behaviour of Hr is quite different and reaction occurs with both named complexes.

Active Site Changes: A pK_a of 11.8 has been obtained for met Hc from spectrophotometric changes.

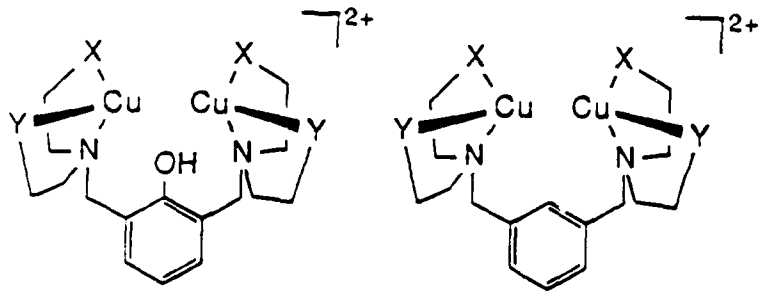
SYNTHETIC MODELS FOR THE ACTIVE SITE OF HEMOCYANIN

T.N. Sorrell, Martha L. Garrity, and Vivian A. Vankai

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA.

The hemocyanins (Hc) are highly aggregated molecules that contain a binuclear-copper active site which functions for many species of marine organisms to bind molecular oxygen for respiration [1]. A crystal structure of deoxyHc shows that each copper(I) ion is coordinated by three imidazole groups from histidine residues [2]; and a variety of spectroscopic studies has further defined the active site structures in several forms of the protein, including oxyHc[3].

The purpose of modeling studies is to confirm the proposed structures for the active site in hemocyanin and to understand the intrinsic properties of the copper-dioxygen interaction [4,5]. Thus, most studies have focused on the synthesis of binuclear copper(I) complexes and those in which the copper(I) ions are coordinated by nitrogen heterocycles. The best studied species are those having pyridine or pyrazole donors; but the synthesis of imidazole-ligated complexes has become increasingly more important. We and others [5] have synthesized binuclear complexes that have six nitrogen donors comprising a combination of imidazole, pyrazole, pyridine,and amino-group ligands:



X = 2-pyridyl
2-(1-methyl)-imidazolyl
2-pyrazolyl

Y = 2-pyridyl
2-(1-methyl)-imidazolyl
2-pyrazolyl

We report the reactivity of these complexes, and their mononuclear analogs, toward dioxygen. Depending on the nature of the donors, we observe no reaction, reversible binding (at low temperature), hydroxylation of the aromatic ring, or formation of hydroperoxide species. The reasons for the different types of reactivity will be discussed as well as the relationship of these results to understanding the structure and reactivity of hemocyanin.

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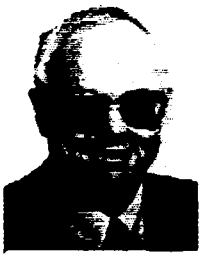
5. Sorrell,T.N. *Tetrahedron* 1989, in press.

BIOGRAPHICAL SKETCHES AND PHOTOGRAPHS

ORGANIZERS

Margo C.A. Balfour: The University of Queensland
The Administration Officer of the Biological Sciences Group of The University of Queensland and Research Assistant to Cliff Hawkins. Margo has had extensive experience in administration, marketing and advertising, and has worked on the Barrier Reef. She is in charge of transport, accommodation, administration aspects, and the conference data base.



Prof. Clifford J. Hawkins: The University of Queensland
Educated at the Newcastle University College of the University of New South Wales (BSc) and the John Curtin School of Medical Research ANU (PhD, DSc). Cliff has been at St. Lucia since 1965. He has worked with Jannik Bjerrum (Copenhagen), Dick Holm (MIT), Ken Raymond (UC Berkeley), Jim Swinehart (UC Davis) and Fred Richardson (Virginia). His research has been concentrated with Cu^{2+}, Cu^{+} redox systems, CD and NMR applications to structural problems, conformational analysis and the chemistry of the Ascidiacea. Cliff is currently the Pro-Vice-Chancellor of the Biological Sciences Group at The University of Queensland, and Professor of Inorganic Chemistry.

Prof. Kenneth N. Raymond: UC, Berkeley
Ken attended Reed College where he received his BA. His PhD at Northwestern University with Fred Basolo and Jim Ibers were concerned with the synthesis and structure of five-coordinate metal complexes. Upon completing his PhD research in 1967 he took up a faculty appointment at the University of California. He was appointed Associate Professor in 1974 and Professor in 1978. He is also an investigator of the Materials and Chemical Sciences Division, Lawrence Berkeley Laboratories. He has been a Vice-Chairman of the Berkeley Chemistry Department and a visiting Professor or Lecturer at several Universities. Professor Raymond has been active in a number areas of coordination chemistry including the siderophores and their models, and the design of sequestering agents specific for individual metals.

B2.

BIOGRAPHICAL DATA

AUSTRALIAN PARTICIPANTS

Prof. Alan M. Bond: Deakin University
Alan is Foundation Professor of Chemistry at Deakin University, Victoria, Australia. He received his BSc, PhD (1971) and DSc (1977) degrees from the University of Melbourne, where he held teaching and research positions. His major research interests involve the development and application of modern electroanalytical techniques.

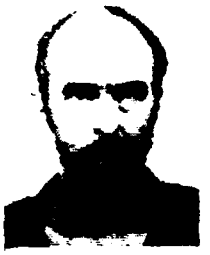
Mr Kevin A. Francesconi: Western Australian Marine Research Laboratories
A graduate of the University of Western Australia, Kevin is a Research Officer at the Western Australian Marine Research Laboratories. His research interests include the biotransformation of metals and metalloids in the marine environment.

Prof. Hans C. Freeman: University of Sydney
Hans has been Professor of Inorganic Chemistry at Sydney University since 1971. He has acted as a Visiting Professor to Universities such as Basel, Göteborg and Yale. Hans has BSc and PhD degrees from Sydney University. He worked with Le Fevre at Sydney and Hughes at CalTech (1954) before taking up an appointment at Sydney University in 1957 where he established a crystallographic laboratory. His recent work has concentrated on protein crystallography.

Dr Keith S. Murray: Monash University

Keith graduated from Manchester University in 1963 (BSc Hons). In 1966 he received his PhD, for his work with Dr D.J. Machin concerning the magnetochemistry of early transition metal ions. Post-doctoral work followed with B.O. West at Monash University, Melbourne, Australia 1966-69 working on metal-Schiff-base chelates with emphasis on μ-oxo-iron(III) compounds. Tenured appointments have been at Monash University: Lecturer 1970; Senior Lecturer 1976; Reader 1985 - present. His research interests include low temperature magnetic and spectral studies of transition metal ions in inorganic and bioinorganic systems and the synthesis, structure and electrical properties of new conducting inorganic solid material.

Dr David L. Parry: University of the Northern Territory



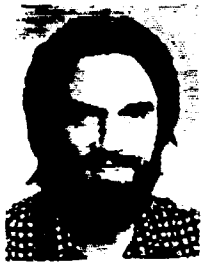
David graduated from the Queensland University of Technology (BAppSc), and holds a DipEd. and a PhD from the University of Queensland. He worked in Cliff Hawkins' laboratory from 1975-1986 mostly on the chemistry and the algal symbionts of the Ascidiacea. He is continuing this work at Darwin, where he holds a lectureship, and is expanding it to include sponges. His other interests include metal accumulation in termite mounds.

Prof. Alan M. Sargeson: Australian National University

Alan studied at the University of Sydney (BSc, PhD). He worked with Frank Dwyer (Sydney and John Curtin School of Medical Research ANU) and with Henry Taube (Stanford). He was one of the foundation appointments to the Research School of Chemistry at the ANU. A Fellow of the Royal Society (London), and an Elected Fellow of the Danish Academy of Science. His research has been concerned with the chemistry of chiral compounds, the mechanisms of substitution and redox reactions, the reactions of coordinated ligands, and the chemistry of cage complexes.

B4.

BIOGRAPHICAL DATA



Dr John Webb: Murdoch University
John graduated with a BSc from Sydney in 1967, a PhD from CalTech in 1972, and a Diploma of Education from Murdoch in 1978. He worked with David Buckingham at ANU before joining the staff at Murdoch in the School of Mathematical and Physical Sciences where he presently holds the position of Senior Lecturer. John's work has been in bioinorganic chemistry, with current interests in the biological mineralization of iron in molluscs and the structure of the iron core in ferritin.

Dr Anthony G. Wedd: La Trobe University
Anthony received his BSc and his PhD from the University of Tasmania. He has held various appointments including Lecturer, Senior Lecturer and Reader in Chemistry at La Trobe University. His research interests involve inorganic synthesis, metalloproteins and physical techniques.

Dr S. Bruce Wild: Australian National University
Bruce graduated from the University of New South Wales (BSc) and the University of Manchester (PhD). After 3 years postdoctoral experience in Germany, the UK and Canada he returned to Australia to take up a Lectureship in the University of Western Australia. He is currently a Senior Fellow at the Australian National University. Dr Wild's research interests to a large extent are concerned with stereochemical studies of phosphorus and arsenic compounds.

US PARTICIPANTS

Prof. Alison Butler: UC, Santa Barbara

Alison Butler received her BA in Chemistry from Reed College in 1977 and her PhD in Inorganic Chemistry from the University of California San Diego in 1982. Professor Butler joined the Chemistry Faculty at UC Santa Barbara in 1986. Her research interests encompass the fields of metallobiochemistry and bioinorganic chemistry with particular emphasis on metalloenzymes that catalyze electron transfer reactions.

Prof. N. Dennis Chasteen: University of New Hampshire

Dennis received his AB from the University of Michigan in 1965, his MS from the University of Illinois in 1966 and his PhD in Physical Chemistry also at the University of Illinois in 1969. He has received various awards and appointments including Visiting Professor at the University of New Hampshire from 1974-1979, and Professor at the University of New Hamsphire from 1979 until present. His research interests include iron storage and transport proteins, applications of EPR and NMR spectroscopy to the study of metalloproteins, and the biochemistry of vanadium.

Prof. Rita R. Colwell: University of Maryland

Rita received her BS (Bacteriology) and her MS (Genetics) from Purdue University. She did her PhD at the University of Washington Seattle, and has received a DSc from the Heriot-Watt University in Edinburgh. She has held positions at Georgetown University, Washington and the University of Maryland, including Vice-President of Academic Affairs at Maryland. Since 1987 she has held the position of Director at the Maryland Biotechnology Institute of the University of Maryland, and Rita is Honorary Professor of Microbiology at the University of Queensland. She has served on committees of the National Academy of Sciences and the NSF, and also holds a Presidential appointment to the National Science Board (1984-90). Rita's research interests include marine biotechnology, marine and estuarine microbial molecular ecology; microbial systematics; marine microbiology; temperature and high pressure effects on marine bacteria and microbial degradation.

B6.

BIOGRAPHICAL DATA

Dr Stephen P. Cramer: Brookhaven National Laboratories
Stephen did his graduate work with Keith Hodgson at Stanford where he also obtained his PhD in 1977, primarily for work done at the SSRL (Stanford Synchrotron Radiation Laboratories). Following a post-doctoral visit with Harry Gray at CalTech in 1978, he spent nearly 8 years at Exxon Research and Engineering Co. He worked at Schlumberger Research from 1986-1988 and recently returned to X-ray spectroscopy full time as a staff member of the NSLS. His current emphasis is on bioinorganic applications of 'softer' X-rays (200-2500 eV) and X-ray fluorescence spectroscopy.

Prof. Alvin L. Crumbliss: Duke University
Alvin received his BA with College Honours from Knox College and his PhD in Inorganic Chemistry from Northwestern University. Following postdoctoral study at the University of Southern California, he joined the faculty of Duke University in 1970 where he is currently Professor of Chemistry. Dr Crumbliss' research interests are in the areas of bioinorganic chemistry, and inorganic and organometallic reaction mechanisms.

Dr James A. Fee: Los Alamos National Laboratory
From 1970-1974 James was Assistant Professor of Chemistry at the Rensselaer Polytechnic Institute. He moved to the University of Michigan where he became Professor of Biological Chemistry & Research Biophysicist. In 1984 he became Director of the NIH Stable Isotope Resource, and Section Leader of Isotope Resource and Structural Chemistry Group at the Los Alamos National Laboratory. James' research interests lie in biochemical/biophysical approaches to structure-function relations in respiratory proteins. He has a developing interest in metal resistant bacteria, with particular emphasis on microorganisms isolated from deep sea hydrothermal vents.

Prof. Peter C. Ford: UC, Santa Barbara

Peter's undergraduate work at CalTech (BS 1962) was followed by graduate study at Yale University where he worked with Kenneth B. Wiberg on organic oxidation mechanisms (PhD 1966). The following year was spent as a NSF Postdoctoral Follow at Stanford University with Henry Taube. In 1967, Peter joined the Department of Chemistry, University of California, where he has held the rank of Professor since 1977. He has held visiting posts at ANU and the H.C. Oersted Institute. Professor Ford's research interests are concerned with mechanistic inorganic and organometallic chemistry with a current emphasis on bioinorganic catalytic activation of small molecules and the photochemistry and photophysics of transition metal compounds.

Prof. Donald M. Kurtz: University of Georgia

Donald graduated with a BSc (1972) from Akron University and with a PhD (1977) from Northwestern University. He held a postdoctoral appointment (1977-79) at Stanford University. He was Assistant Professor at Iowa State University, and currently is an Associate Professor at the University of Georgia. Donald's research interests include bioinorganic chemistry, chemistry and spectroscopy of metal sites in various proteins.

Prof. Richard H. Holm: Harvard University

Richard holds a BS degree from the University of Massachusetts and a PhD from Massachusetts Institute of Technology. He started his academic career as an assistant professor at Harvard University and subsequently served on the faculties of the University of Wisconsin, M.I.T., and Stanford University. In 1983 he became Higgins Professor of Chemistry at Harvard University. Holm is a member of the American Academy of Arts and Sciences and the National Academy of Sciences. His research interests are in the chemistry of the transition elements including synthetic analogues and reaction systems of the active sites of cytochrome P-450, iron-sulfur proteins and enzymes, molybdenum hydroxylases, and the Mo- and V- containing sites of nitrogenases.

B8.

BIOGRAPHICAL DATA

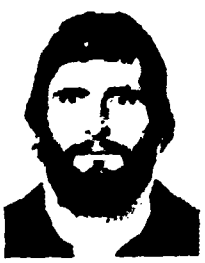
Prof. Kenneth Kustin: Brandeis University
Ken graduated from Queens College (BSc) and from the University of Minnesota (PhD). He received a Postdoctoral Fellowship to study with Manfred Eigen at the Max Planck Institut für Physikalische Chemie in Gttingen. He is currently a Professor of Chemistry at Brandeis University. He also studied NMR with Robert Connick at the University of California and, as a visiting Professor of Pharmacology, he attended Harvard Medical School. Recently he has contributed to the design and mechanistic elucidation of oscillating reactions and to the study the role of vanadium in biological systems, especially in sea squirt blood cells.

Prof. Stephen J. Lippard: Massachusetts Institute of Technology
Steve attended Haverford College (BA) and MIT (PhD). He has worked with Al Cotton (MIT); Bo Malmstrom (Goteborg), Aaron King (MRC Lab. Cambridge) and W. Herrmann (Tech. University, Munich). Steve held a faculty appointment at Columbia University. In 1983 he moved to MIT where he currently holds the Arthur Amos Noyes Chair of Chemistry. Steve is a fellow of the American Academy of Arts and Sciences and is the recipient of many awards for his work on the inorganic chemistry of Fe-proteins and the model of action of platinum anti-cancer agents.

Prof. Francois M. Morel: Massachusetts Institute of Technology
Francois received his MA (1966) from the Universitè de Grenoble. He then went on and received his Dip. d'Ingenieur Hydraulicien (1967) from Grenoble, MS (1968) and also his PhD (1971) from CalTech. He has held the positions of Research Fellow at CalTech, Associate Director for Research at Ecole des Mines de Paris, and Associate Professor at the Sorbonne. His research interests include the interaction of metals in aquatic systems with particles and with ligands.

Prof. Vincent L. Pecoraro: University of Michigan
Vincent received his BS in Biochemistry at UCLA (1977) and his PhD in Inorganic Chemistry with Ken Raymond at UC, Berkeley with his Postdoctoral in Enzymology being completed at UW, Madison with W.W. Cleland. He is currently an Associate Professor of Chemistry at the University Of Michigan. His research interests include the definition of the active site structure and chemical mechanism of manganese containing enzymes; evaluation of biological long-range electron transfer using proteins modified by site-directed mutagenesis and metalloprotein transport and processing into organelles.

Prof. Cortlandt Pierport: University of Colarado
Cort completed his undergraduate studies at Columbia University with a major in Chemistry in 1967 and entered graduate school at Brown University in Richard Eisenberg's laboratory. He graduated with a PhD in 1971 and moved to West Virginia University as Assistant Professor, and then in 1975 to the University of Colorado where he is currently Professor, and Chairman of the Department of Chemistry and Biochemistry. Research activities have been in the areas of organometallic and coordination chemistry, including coordination properties of quinone, semiquinone, and catechol ligands.



Prof. Christopher A. Reed: University of Southern California
Chris was educated in New Zealand with a BSc, MSc, and PhD from Auckland University. Chris worked with Warren Roper in Auckland for his research degrees and then with Jim Collman at Stanford from 1971-1973. He joined the faculty of USC in 1973 and was appointed Professor of Chemistry in 1982. He has held visiting posts at Grenoble, Auckland and Monash. His research interests cover areas of iron and copper bioinorganic chemistry, antiferro- and ferromagnetically interacting centres, and organometallic chemistry including novel routes to coordinatively unsaturated complexes.

B10.

BIOGRAPHICAL DATA

Prof. Jonathan L. Sessler: University of Texas
Jon received his BS degree from UC Berkeley, and his PhD from Stanford (Jim Collman). He has held postdoctoral appointments with Jean-Marie Lehn at Strasbourg, and with Iwao Tabushi in Kyoto. He accepted the faculty position of Assistant Professor of Chemistry in 1984 at the University of Texas Austin. His current interests include bioinorganic chemistry, especially hemoprotein molecules, and molecular recognition.

Prof. Thomas N. Sorrell: University of North Carolina
Tom received his BA in Chemistry from New College, Florida and his PhD in Organic Chemistry with Jim Collman at Stanford University, California. From 1977-1983 he was Assistant Professor at the University of North Carolina and in 1983 was appointed Associate Professor at the University. His research interests currently involve the copper proteins, hemocyanin and tyrosinase.

Prof. James A. Swinehart: UC, Davis
Jim received his BA from Pomona College (1958), did his graduate work at the University of Chicago with Henry Taube (PhD 1962), and postdoctoral work at the Max Planck Institute for Physical Chemistry in Göttingen. His research interests involve the mechanisms by which pollutants interact with biological systems, unusual metals in marine organisms, chemical solutions to environmental problems, the origins of color in minerals, and inorganic reaction mechanisms. Jim has participated in exchange programs at the University of Chile and the University of Queensland.

Prof. Elizabeth C. Theil: Northern Carolina State University

Liz is a Professor of Biochemistry at North Carolina State University, Raleigh. She is an expert in the study of the ferritin family of proteins. Her particular emphasis has been on the formation and structure of ferritin iron cores and models, cell-specificity of ferritin protein structure and gene expression (particularly during development), and ferritin mRNA structure and function (translational control). She has an interest in single cell organisms as possible models for ancient or unusual modes of iron storage.

Prof. Teddy G. Traylor: UC, San Deigo

Teddy graduated from UCLA in 1949 with a BA in Chemistry and in 1952 with a PhD in Organic Chemistry. His supervisor of his doctoral research was the late Saul Winstein. After 6 years at the Dow Chemical Company he was a NIH postdoctoral fellow with Paul D. Bartlett at Harvard University. He joined the Chemistry Department at UCSD in 1961 and became Professor of Chemistry in 1968. He has collaborated with Eraldo Antonini, Maurizio Brunori, David Dolphin, James Ibers and others. His current research interests include oxygen transport and activation by heme and nonheme metalloproteins, and general bioinorganic chemistry as a student with synthetic analogues of biological molecules.

Prof. J. Herbert Waite: University of Delaware

Herbert received an AB degree with a major in Biology from Harvard College, and a PhD in Zoology from Duke University. At the University of Connecticut he held an Assistant Professorship in the School of Medicine from 1981-86. He moved to the College of Marine Studies at the University of Delaware in 1986. He has done pioneering research on the isolation and characterization of DOPA-proteins from various marine invertebrates.

BIOGRAPHICAL DATA

OTHER COUNTRY PARTICIPANTS

Prof. William R. Cullen: University of British Columbia
Bill gained a BSc and MSc at the University of Otago, Dunedin, before traveling to Cambridge, England, to work with Professor J.H. Emleus on the trifluoromethyl derivatives of arsenic. He finished his PhD work in 1958 and was appointed to the faculty at the University of British Columbia where he has remained since, apart from time spent as a visiting professor in Universities in England and Australia. Bill continued his early interest in the Chemistry of arsenic throughout his career with emphasis on the isolation, identification, biochemistry and toxicology of compounds of arsenic, as well as antimony and tin, from the marine environment. His other interests are in asymmetric hydrogenation and organometallic synthesis.

Prof. David Dolphin: University of British Columbia
David received his BSc (1962), PhD (1965), DSc (1982), at the University of Nottingham, England. He was a Postdoctoral Fellow with R.B. Woodward, Harvard University, 1965-66. He joined the Faculty at Harvard 1966 and left in 1973 as an Associate Professor. David moved to his present position at the University of British Columbia where he is currently Professor of Chemistry and Acting Dean of Science. His research is principally in the area of tetrapyrrolic macrocycles (porphyrins, vitamin B_{12}).

Prof. A. Geoffrey Sykes: University of Newcastle upon Tyne
Professor Sykes has BSc, PhD and DSc degrees from the University of Manchester. Post-doctoral years were at Princeton and Adelaide Universities. After a period at the University of Leeds as Lecturer and Reader, he became Professor of Inorganic Chemistry at the University of Newcastle upon Tyne in 1980. His interests are in transition-metal coordination chemistry, inorganic and bioinorganic (metalloprotein) mechanisms.

Dr Hans Vilter: *Friedrich Wilhelms University*

Hans studied at the Fredrich Wilhelms University gaining his doctorate in 1980. He has worked at the Zoological Research Institute and Museum Alexander Koenig in Bonn, the Institute of Pharmaceutical Biology at the University of Bonn. His research has been concerned with marine algae, bacteria and fungi, especially the isolation of antibiotic efficacious substances, alginate splitting enzymes, and vanadium haloperoxidases.

Prof. Ronald Wever: University of Amsterdam

Ron started studying chemistry in 1965 and received his PhD in 1975. In the same year he joined the staff of the Laboratory of Biochemistry at the University of Amsterdam. His research is centered on metalloproteins and redox reactions involving oxygen and oxygen intermediates (hydrogen peroxide, superoxide). The enzymes and systems studied include cytochrome c oxidase, haemoglobin, copper proteins like superoxide dismutase and ceruloplasmin, the O_2^- generating system from leucocytes, myeloperoxidase, eosinophil peroxidase, lactoperoxidase, bromoperidases from various origins and more recently the novel vanadium-containing bromoperoxidases from seaweed and the production of halogenated intermediates by these seaweeds.

Prof. Karl Wieghardt: Ruhr University, Bochum

Karl studied chemistry in Hamburg and Heidelberg. His PhD was received in 1969 under the supervision of Professor H. Siebert. He has held a post-doctoral fellowship with Geoff Sykes at Leeds in 1972-73, a junior lectureship at the University of Heidelberg, an associate professorship at the University of Hanover (1975-1980), and the Chair of Inorganic Chemistry at the Ruhr University, Bochum. His research interests are bioinorganic chemistry, inorganic reaction mechanisms, and macrocyclic transition metal complexes.

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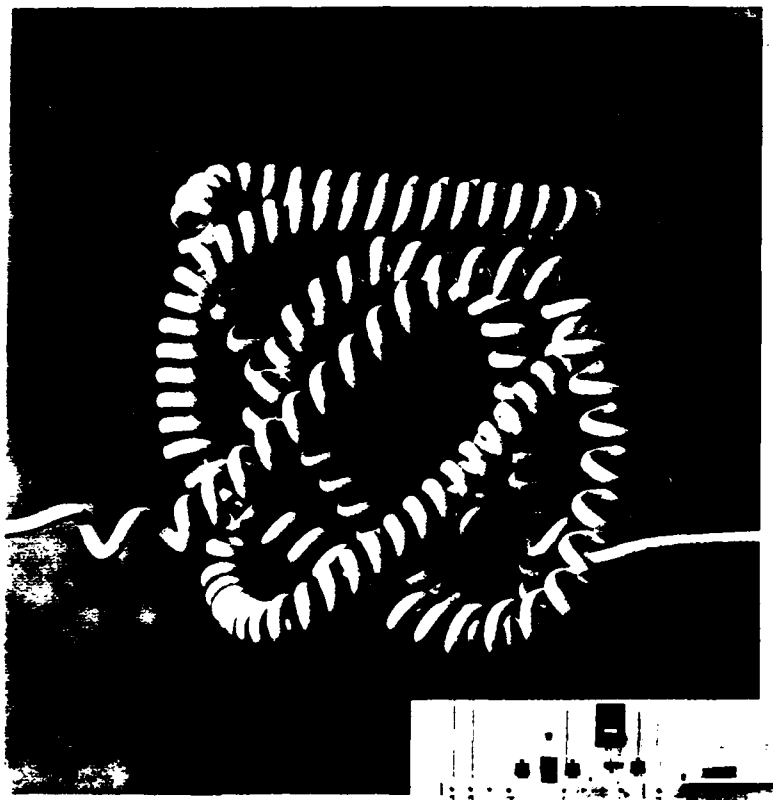

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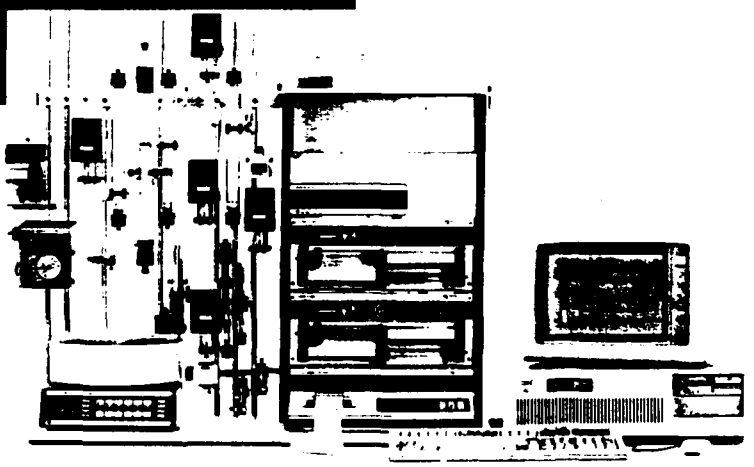

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n the Great Barrier Reef

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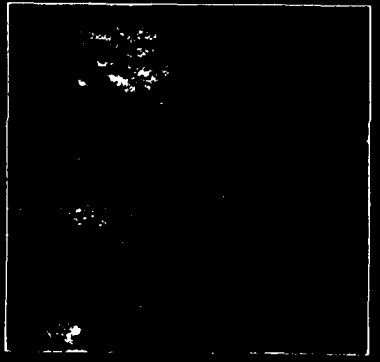

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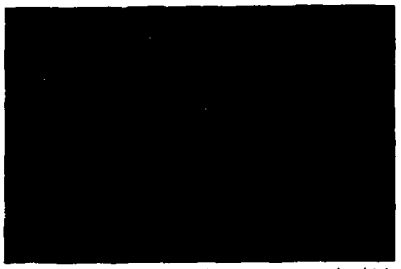
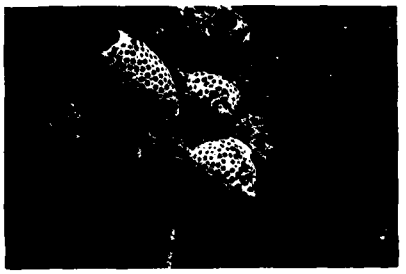


1. CALCAREOUS ALGAE This green seaweed, which is abundant in lagoons and sandy reef slopes, secretes a calcium carbonate skeleton. When it dies, the skeleton crumbles adding to the sand around reefs.

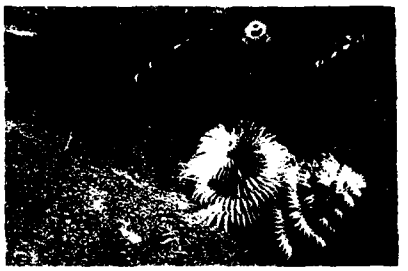
2. TURTLE WEED This green alga grows in clumps up to about 100 mm high. Here it is growing on *Porites* coral. Despite its name, it is not often eaten by turtles or fish as it contains toxic terpene chemicals.

3. STINGING HYDROID A colonial relative of the jellyfish and corals, its feeding individuals (polyps) have many stinging cells for capturing prey and for defence. A brush with this hydroid can be painful, like brushing a stinging nettle, but not deadly.

4. PINK SPONGE Sponges are abundant and important members of the reef community. They sieve tiny animals and plants (plankton), mucus and other waste products from the water, retaining energy in the community. Many sponges also farm plants (zooxanthellae).



5. COMPOUND SEA SQUIRT The sea squirts are also abundant in the reef community. They resemble sponges as adults but, when young, they look more like fish. Like clams, corals and many sponges, they contain symbiotic algae. They also feed by filtering plankton.



6. CHRISTMAS TREE WORMS These brilliantly coloured tubeworms live in the massive corals, particularly the intertidal microatolls. The coral grows around their tubes, giving them added protection. Only their spiral gills are exposed to obtain oxygen and floating food.

7. HERMIT CRAB Crustaceans on the reef may be extremely vulnerable to predators. Many emerge at night only or live in association with corals or other animals. The hermit crab protects its soft abdomen with a borrowed snail shell.

8. TEXTILE CONE SHELL This mollusc (marine snail), shown here with its eggs, has a venomous sting for capturing its prey (other molluscs). Some cone shells are dangerous to humans and all should be handled only with great caution.

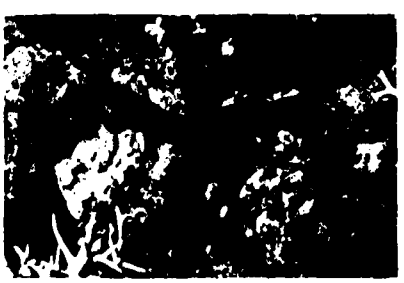
9. SPIDER SHELL This active mollusc has been turned over to show its two eyes and the muscular foot ending in a claw which is used for protection and for stability. It inhabits shallow lagoons, feeding on algae.

10. SEA SLUG Called a nudibranch, this shell-less mollusc has naked gills on the back of its body. Many nudibranchs are brilliantly coloured and distinctively patterned such as this one which has just laid a bright yellow collar containing thousands of eggs.

11. GIANT CLAM This gigantic bivalve (two-shelled) mollusc is aided in its spectacular growth by the garden of microscopic plants within its fleshy mantle. The largest giant clam grows to over 1 metre long and may weigh hundreds of kilograms.

12. SEA CUCUMBER A relative of the starfish, feather stars and sea urchins, the sea cucumber lies on its side ingesting organic matter from the sand and reef surfaces. Some emit sticky white threads as a defence mechanism when disturbed.

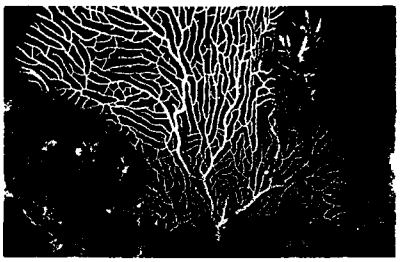
13. FEATHER STAR This relative of the starfish and sea urchins spreads its arms to catch floating plankton which is then passed along the arms to the mouth.



14. BLUE STARFISH Usually lives on reef tops where it feeds on microorganisms and other food fragments on the reef surface.

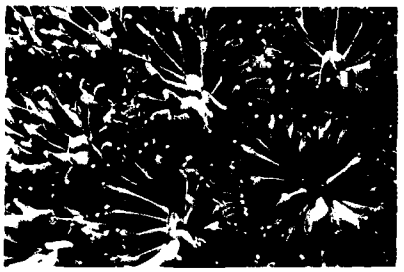
15. CROWN OF THORNS STARFISH A large starfish with about 16 arms, it feeds on living coral tissue, leaving only the skeleton behind. Sometimes occurs in great numbers causing much damage to reefs. The reasons for the outbreaks are not known.

16. FIRE CORAL This hydrozoan is a closer relative of the jellyfish than of the true corals. Its polyps are specialised for different functions such as feeding or defence and can give a sting to a human skin.

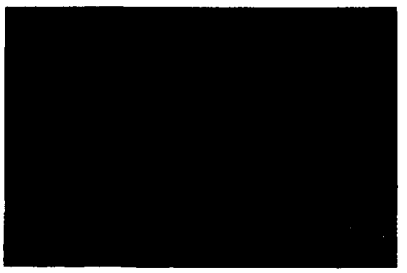


17. GORGONIANS Related to the soft corals, the gorgonians or sea fans have a horny skeleton. They are found in deeper water usually in areas of high current.

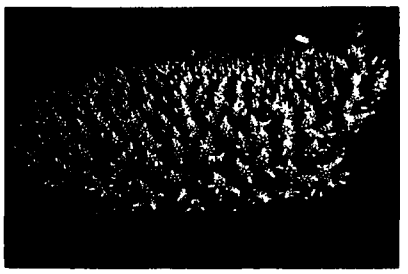
18. SOFT CORALS Soft corals lack the rigid calcareous skeleton of the reef-building hard corals. With its polyps expanded, the colony on the left has a feathery appearance. With polyps withdrawn into its rubbery matrix, the colony on the right appears smooth.



19. HARD CORAL POLYPS The coral animal, the polyp, is a soft bag with a mouth and stomach surrounded by a ring of stinging tentacles, all held in a limestone cup. It feeds on plankton but obtains most of its food from plants (zooxanthellae) housed in its tissues.

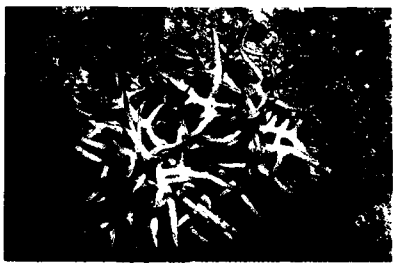


20. BRANCHING STAGHORNS These delicate corals are found in lagoons where wave action is minimised. They are fast growing and provide important shelter for reef fish.



21. STAGHORN CORAL This is the only coral form to have a single polyp on the tip of each branch. Colony sizes range from a few centimetres to several metres across and, in some areas, thickets of staghorn coral extend over hectares.

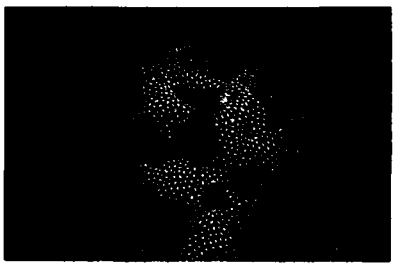
22. PLATE CORAL A close relative of the staghorns, plate coral is made up of many short branches all joined at the base.



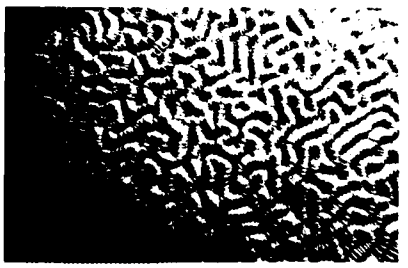
23. NEEDLE CORAL Thin fragile branches are constructed by hundreds of small polyps. They protude at night from the tiny holes which can be seen on each branch

24. SMOOTH KNOBBY CORAL Here the holes into which the polyps have contracted can be seen more easily. The coral skeleton consists of limestone, extracted chemically from sea water by the polyps with the aid of their plant partners.

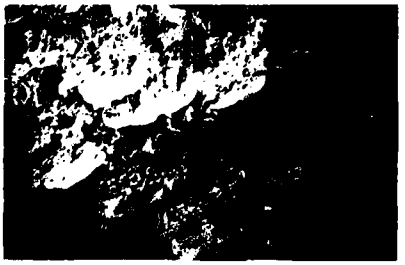
25. LEAF CORAL In deep water where there is less light, corals tend to flatten out and become delicate leafy shapes.



26. HONEYCOMB CORAL These massive or rock-shaped corals have their individual polyps separated by circular walls, but all polyps interconnect by a thin layer of tissue.



27. BRAIN CORAL The polyps have joined their walls together to form ridges and the valleys contain a row of polyp mouths.



28. ENCRUSTING CORAL Encrusting forms of several hard corals exist. They compete well for space and light growing over neighbouring corals and other sedentary organisms

29. MUSHROOM CORAL This coral is unusual as it is a single giant polyp and does not attach to the reef floor. The tentacles expand at night

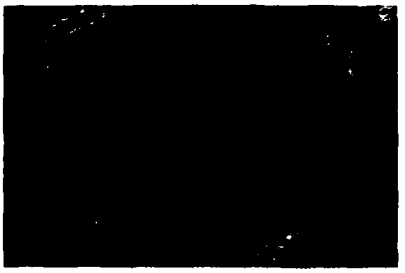
30. MUSHROOM CORAL This second type of mushroom coral has very long tentacles which remain extended day and night.

31. BLUE PULLERS These abundant and conspicuous damselfish are plankton feeders and hover close to stands of staghorn corals. When threatened, they pull *into the coral for cover. (Grow up to 110 mm long)*

32. ANEMONE FISH This specialised damselfish gains protection from and is immune to, the paralysing anemone tentacles among which it swims freely. (Grows to 140 mm)

33. BUTTERFLY FISH Colourful, flat and deep-bodied fish usually found in pairs. They feed on small crustaceans, algae, and/or coral polyps. (The largest of the butterfly fish reaches 300 mm. Several species grow only to about half that length.)

34. TRUMPET FISH Long, slender fish with a distended trumpet-like mouth used to seize small fish. A habit of swimming just above a coral trout to give the image of one large fish, helps it sneak up on its prey. (Grows to 750 mm or more.)



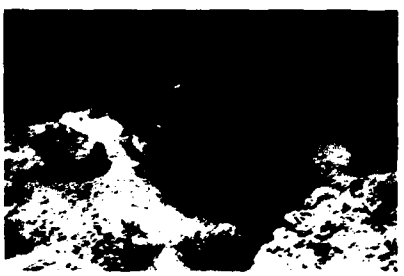
35. PARROT FISH Brightly coloured, heavy-bodied fish with beak-like jaws used to break off algae and coral. The sound of parrot fish crunching can often be heard, particularly on the reef flat at high tide. They swim distinctively, using only their pectoral fins. (Common species grow to between 350 mm and 1 metre)

36. CORAL TROUT Large predatory fish related to the gropers and rockcods. Commonly feeds on small schooling fish and is a highly esteemed table fish. (Six species found on the Reef grow to between 500 mm and 1 metre)

37. SWEETLIP A large, deep-bodied, and often conspicuously-coloured fish with extremely thick and fleshy lips. Feeds on shelled animals and worms vacuumed from the sand. (The largest of the sweetlips grows to about 900 mm)

38. ANGEL FISH This brightly-coloured, disc-shaped grazer usually lives in pairs. Other smaller angel fish live in groups with one male and a harem of females. (This species grows to 380 mm)

39. CLEANER FISHES Small, striped, cigar-shaped fishes which clean dead tissues and parasites from the skin, mouth and gills of other fish — here a damselfish. Large fish suspend their predatory impulses for this cleaning treatment! (Grow to 100 mm)



40. LAGOON RAY This cartilaginous fish feeds on molluscs and crustaceans in the sand. Often partially buried in the sand, its two venomous tail barbs pose a threat to beach bathers. (Commonly has a disk about 800 mm in diameter and a total length of 900 mm, but known to reach a length of 2.4 m)

41. WHITE TIP SHARK A common reef shark which seldom reaches more than 1-2 metres long. As scavengers, they are normally harmless to humans.

42. GREEN TURTLE A marine reptile which forages for algae and sea grasses. The female comes onto sandy coral cays to lay her eggs at night.

Photos: REEF BIOSEARCH (1, 2, 4, 12, 16, 18, 25, 26, 27, 29, 30, 31, 32, 33, 35, 36, 37, 40); R & V Taylor (3); Neville Coleman (8); Nev Collins (42); GBRMPA

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June 1988

other, less familiar, creatures. This immense variety of invertebrate life forms provides a backdrop to some 1 500 species of fish of all descriptions.

The Reef is also the breeding area for a number of rare and endangered animal species. Humpback whales come from the Antarctic to give birth to their young in Reef waters. Six of the world's seven species of sea turtle breed on the Reef, and dugong make their home among the sheltered seagrass beds.

For some people the Great Barrier Reef is their livelihood. Reef waters, which support an abundance of prawns, fish and scallops, sustain an important Queensland commercial fishing industry.

The Reef Region is fast becoming a major tourist destination. The advent of high-speed, large capacity catamarans now provides tourists with access to areas of the Reef which were once only visited by a privileged few.

To the master of a ship or a yachtsman, the Great Barrier Reef may be a formidable obstacle to navigation. In most places the Reef is many kilometres from the coast, but the waters within the outer barrier are also studded with submerged shoals and reefs. Added to this are the strong trade winds and occasional cyclones which are characteristic of the Region. Sailing the Barrier Reef is often a test of navigational skill.

For other people, the Reef is a place for enjoyment and relaxation, where they come to wonder at the beauty and strangeness of this natural world. Whether snorkelling, diving or catching a fish for the family table, the Reef is a marvellous place for recreation.

To scientists, the Reef is a place of never ending fascination. They study its weather, its water currents, its geology, its chemistry and its plants and animals, in an attempt to discover how this immense and amazing system works.

How are coral reefs made?

The living, growing portion of a coral reef is a thin veneer on the surface of the cemented limestone skeletons of millions of dead corals and the remains of limestone producing (calcareous) plants. The reef cement is partially formed by encrusting algae, and partially by chemical precipitation from the water.

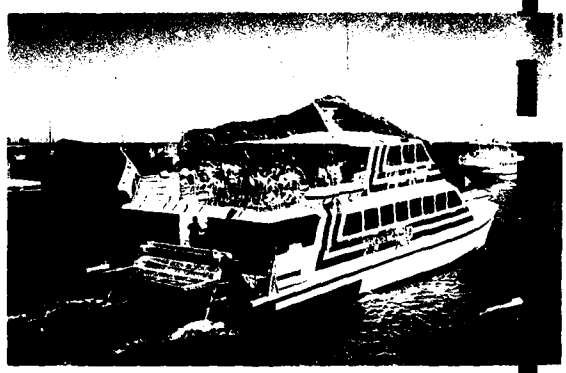
Coral polyps, with the help of single-celled plants (zooxanthellae) living within them, convert dissolved limestone from the water into hard limestone. Polyps build their communal limestone homes into a multitude of shapes and sizes to produce the complex and beautiful coral colonies we see underwater. Coralline algae and calcareous sponges grow between the old coral colonies and help cement them into solid reefs.

Reef building corals need warm waters in which to grow and their plant helpers, the zooxanthellae, need light, just as plants on land do. For this reason, coral reefs only develop well in warm, shallow and clear tropical seas.

From top—

Commercial fishing is a major Reef industry and takes many forms. Scallops are caught mainly in the southern part of the Reef.

A pleasant day on the Reef is crowned by a prize catch. It has been estimated that more than a third of Queenslanders participate at least occasionally in recreational fishing and it is probably the most popular recreational activity on the Reef.



Increasingly, high-speed catamarans are the vessels preferred by the tourism industry. Travelling at up to 30 knots they provide visitors with access to areas of the Reef previously seen by only a privileged few. Photograph courtesy South Molle Island.

More and more people are enjoying the pleasures of exploring coral reefs. Hardy Reef, Central Section.

The Great Barrier Reef

Reefs and islands

Reefs are not all the same shape and size. Three major types of reefs are found on the Great Barrier Reef: ribbon reefs, fringing reefs and patch reefs. Ribbon reefs occur in the northern part of the Great Barrier Reef. They are relatively narrow walls on the edge of the continental shelf and form a broken barrier with passages between the individual reefs. Some of these passages are large enough to allow ships through.

Fringing reefs may develop off the sloping sides of continental islands or along the mainland coast. Patch reefs are usually round or oval and grow like platforms on the continental shelf.

As well as these fairly common reef types, there is a bewildering range of others. For example plug reefs are triangular in shape with the point towards the ocean, while deltaic reefs are cut by channels and resemble river deltas. Other shapes may develop in response to particular combinations of geological, meteorological and biological conditions.

As a reef develops, wave action and storms may smash corals along its edge, throwing the resulting rubble up onto the reef. Further water movement, tumbling, and the action of boring organisms reduces some of the pieces to coral sand. Much more sand is made directly by calcareous green algae and tiny forams (single-celled animals with calcareous shells), and by the crumbling of encrusting red algae. The sand is often swept off the reef into a lagoon or back-reef, but a visible sandbank (or cay) may form on the reef, exposed at low tide. Such cays appear on many reefs, shifting, growing larger or washing away at the whim of sea, tide and wind. If the cay enlarges with the accumulation of more coral debris, it may become a resting site for seabirds. When the cay is built up to the point where it remains exposed above the sea at all times seeds may germinate and vegetation will appear. In this way a vegetated cay may develop.

Centre—
The steep cliff line of eroding rock around a continental island (North Direction Island, near Lizard Island) contrasts with the platform-like growth of fringing reef stretching out from the island just below sea level.

Top—
Sand cays are the most common island type on the Great Barrier Reef. These piles of sand dumped on the sheltered parts of reef tops are often mobile in their early stages of development, changing shape with wind, wave and tide.

In time some cays are colonised by a succession of invading plants. Low creepers are usually the first to arrive, helping to stabilise the cay. Eventually a dense forest may develop, as here on Bushy Island near Mackay.

Right—
These green algae **(Halimeda spp.)** *often resemble terrestrial plants and play the same light capturing role. But in common with a number of other reef algae — many of which more closely resemble pinkish cement than any plant we are used to — they contain limestone material which is left when they die (centre of photograph). In time collections of these plate-like particles break up and add to the supply of sand found on and around coral reefs.*

The Marine Park

The goal of the Great Barrier Reef Marine Park Authority is to provide for the protection, wise use, appreciation and enjoyment of the Great Barrier Reef for all time.

The Authority aims to achieve its goal through creating a Marine Park. This Park allows all people — whether they be fishermen, tourist operators, holiday makers, divers, scientists or others — to continue to use the Reef in ways which do not damage it.

To this end the Authority prepares zoning plans for each section of the Marine Park. The object of a zoning plan is to separate potentially conflicting uses while allowing most activities to continue at a level which the resources of the Reef can support. In preparing a zoning plan, the Authority seeks information from reef users, scientists, government departments and the general public. This information is used to produce a zoning plan which allows the maximum wise use and enjoyment of the Reef without threatening its long term survival.

The Great Barrier Reef and you

The Great Barrier Reef is an important part of Australia's, and indeed the world's, heritage. Its continuing good health depends on the care and concern of all those who use it. The Great Barrier Reef Marine Park Authority hopes that whatever your contact with the Reef, it is both enjoyable and rewarding.

This Reef Note has introduced the Great Barrier Reef in general terms. Several of the topics touched on are discussed in greater detail in other Reef Notes.

A sought after aquarium specimen, the blue angel fish, **Pomacanthus semicirculatus,** *is just one of around 1 500 species of fishes of all shapes, colours and sizes that live in Reef waters.*

Marine Parks

Great Barrier Reef Marine Park Authority

Queensland National Parks and Wildlife Service

This Reef Note is one in a series published by the Great Barrier Reef Marine Park Authority and the Queensland National Parks and Wildlife Service to promote a better understanding of the Great Barrier Reef.

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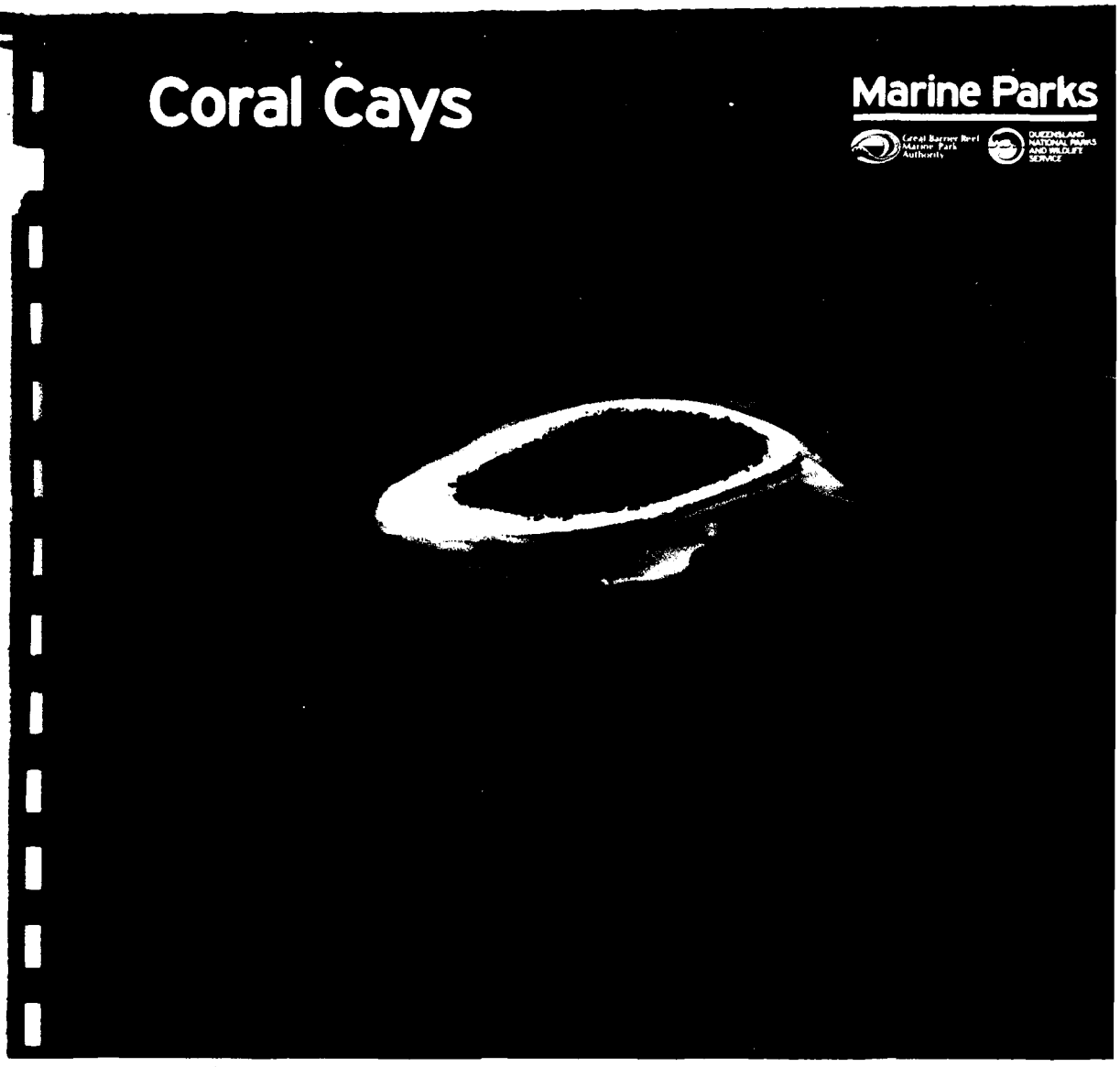
Coral Cays

Marine Parks

Great Barrier Reef Marine Park Authority

Queensland National Parks and Wildlife Service



Cays may be classified according to their shape, vegetation and sediment types. Bushy Island on Redbill Reef near Mackay is a typical Great Barrier Reef sand cay with dense Pisonia forest, a wide beach of coral debris and a dark band of protective beach rock. Similar cays of Green and Heron Island have been developed as tourist resorts.

Coral cays

A coral cay is a 'low' island formed entirely from the sedimentary debris created by the reef on which it stands, sediments which have been swept into a particular part of the reef by wave action. No continental rocks are associated with coral cays which are thus clearly differentiated from the 'high' islands with fringing reefs usually found closer to the mainland.

Once an initial shingle bank has formed, subsequent storms may build up further shingle ridges which in time become vegetated. Only a handful of such islands are found on the Great Barrier Reef, most occurring in the south — including One Tree Island and here at Lady Elliott Island.

The formation of a coral cay

As the plants and animals which form and live on a coral reef die, the smaller skeletons and debris are swept by waves towards the leeside of the reef. Larger coral boulders and particularly shingle formed mainly from the broken sticks of branching corals may be deposited closer to the windward side of the reef. However, unless the sweeping action of the waves concentrates the debris into a particular part of the reef flat, no island can form and instead, as is the case on many reefs, only a scattered area of rubble occurs on the windward side of the reef, grading into a sand sheet to the lee.

Sometimes the shape of a reef and its orientation to the prevailing waves results in bending or refraction of the wave fronts as they move into the shallow waters of the reef flat. This causes the sand or shingle to be swept into a particular part of the reef flat. This concentration of sediment is the initial stage in cay formation. It is helped by the reef having a regular oval shape which concentrates the pattern of wave refraction in a particular area and by low to moderate tidal range which will mean that the wave pattern at all stages of the tide will be similar. A large area of reef flat is not necessary and some cays form on small patches no larger than a football field. However, at any stage in cay formation, the concentrated sediments may be scattered over the reef flat by tropical cyclones and take many years to recover their former concentrated form.

Hoskyn Reef has both vegetated sand and shingle cays. The open ocean swells from the Tasman Sea and cyclone activity concentrate the larger coral fragments which form the shingle cay. Finer sediments which are moved to the leeside under less stormy conditions form the sand cay.

Coral Cays

Stabilisation and development

Initially the embryo cay is little more than an unstable sand bank, changing its position on the reef flat by tens of metres with every change in weather conditions. As it increases in size, however, such movements become smaller and while changes to the shape of the cay may still take place, its position on the reef becomes more stable. King tides may build it up to levels which are overlapped only a few times a year and seabirds may begin to nest on its crown.

Seabirds are important for they bring in seeds of plants either attached to their feathers or within their digestive tracts. Many early colonising plants of cays also have seeds which float and are still capable of germination when washed up onto a cay after as much as 90 days at sea. This initial vegetation is usually in the form of low creepers which further help to stabilise the sand surface of the cay and in particular may help in the trapping of wind blown sand. This gives the young island a dune capping which may now rise above the highest tides.

The colonising vegetation adds organic matter to the raw sands of the cay and the developing sandy soils may also be enriched by the phosphatic guano from nesting seabirds. However, particularly when the vegetation is low, bird droppings may be detrimental to the plants which may become stunted or even die. In time rainfall carries the guano down into the cay where phosphates may cement the cay sands into a hard pan known as cay sandstone. Some cays of the Great Barrier Reef were mined for this source of phosphate towards the end of the last century, the excavated pits still being clearly visible on these islands. The cay sandstone, however, has an important function in further stabilising the cay against movement or erosion. Even more important in this respect is the formation of beach rock. Beach rock forms when calcium carbonate precipitates out of the groundwaters of the cay and cements together subsurface beach deposits. The cemented deposits form a concrete-like ramp which clearly displays the bedding of the cay sands and which acts as a very effective buffer against erosion.

These features continue to increase the stability and size of the cay. Once the cay exceeds an area of a few hectares a freshwater lens, a

There are over 200 unvegetated sand cays, such as Wheeler Cay (pictured) off Townsville. They vary from highly mobile sandbanks to substantial islands with beach rock only just topped by waves. Found on the leeside of a reef they are the most common island type in the Great Barrier Reef.

Sixty-five vegetated sand cays occur in the Barrier Reef Region. Some have only one or two species of herbaceous or salt tolerant plants. Others such as East Hope Island (pictured) have up to forty species including rainforest trees.

Pipon Reef off Cape Melville is one of approximately forty-five low wooded islands which are a special type of cay found only north of Cairns on the Great Barrier Reef.

Low wooded islands consist of a leeward sand cay and extensive shingle ridges around the reef margins enclosing a central reef flat area which has been colonised by mangroves.

small natural reservoir of groundwater, may become a permanent feature beneath the cay. This allows further species of plants, particularly trees, to become established. However, no cay can be regarded as completely stable. Changes are constantly taking place, particularly at the narrower ends of cays where unvegetated spits may alter position on almost every tide. Passage of a tropical cyclone may completely erode even a large cay with beach rock; several reefs in the Great Barrier Reef show the location of former cays outlined on the reef flat by only a narrow band of beach rock.

Age and distribution

Coral reef cays are geologically young. They developed only in the last 6000 years or so since sea level rose to its present position from its low stand of the last great Ice Age. Only when sea level stabilised was it possible for reef flats to expand and provide potential sites for the formation of cays. This fact has important ecological implications, for cays are the established nesting sites of numerous species of birds and turtles. Such sites would have been very restricted before 6000 years ago.

Cays are not uniformly distributed over the Great Barrier Reef. Vegetated shingle cays are found only on southern reefs open to Tasman Sea oceanic swells. Low wooded islands are found only north of Cairns and close to the mainland because their development requires low wave energy conditions and colonisation by mangroves from the nearby mainland. Vegetated sand cays are found only on the northern Great Barrier Reef north of Cairns (Green Island is the southernmost of this group) and on the southern Reef south of about Mackay. The entire central Great Barrier Reef, for a distance of 640 kilometres, is devoid of vegetated cays and even unvegetated cays are rare. The reasons for this are complex. The irregular shape of many reefs in this area may not refract waves in a way that concentrates reef debris. Also tropical cyclones, which can scatter concentrated sediments over a reef flat, reach their greatest strength and frequency on the central Reef. In addition, the tidal range on the Great Barrier Reef is greatest in the south central region, a factor which acts against sediments being deposited in a particular part of a reef as wave patterns at high and low tides may be very different.

Banks or linear tongues of shingle may be deposited close to the windward margins of many reefs during storms as shown here on Pandora Reef. The open nature of the shingle is not favourable for water retention and colonisation by plants is slow.

Author

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This Reef Note is one in a series published by the Great Barrier Reef Marine Park Authority to promote a better understanding of the Great Barrier Reef.

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Marine Parks

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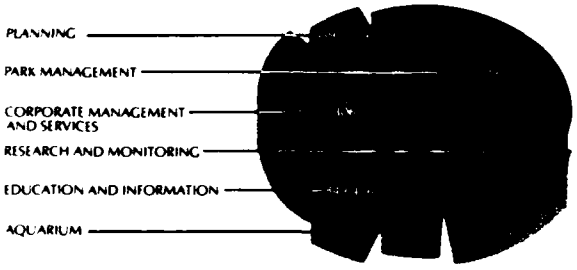
provide interpretive services as well as enforcement, surveillance and other management activities.

Surveillance of the Marine Park, larger in size than the state of Victoria or Great Britain, is a difficult task and requires the support of many resources. Aircraft fitted with sophisticated equipment, operated by Coastwatch and the Q.NPWS cover the entire Great Barrier Reef Region at frequent intervals.

World Heritage Listing recognised the Reef, not only within Queensland, or even Australia, but throughout the world, as a very special place. Because of its outstanding universal value, the Great Barrier Reef was inscribed on the World Heritage List in 1981 under the UNESCO Convention

EXPENDITURE OF FUNDS BY PROGRAM 1986-87

(TOTAL EXPENDITURE $8 225 820)

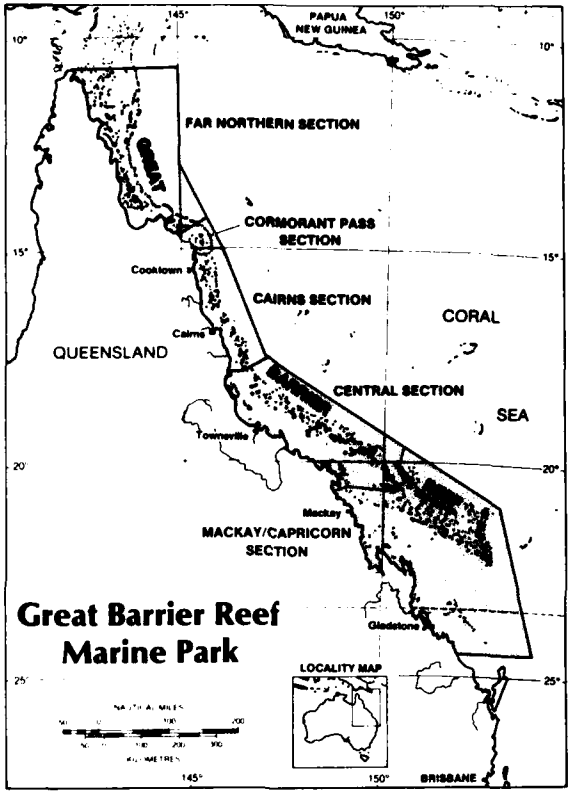


concerning the protection of the World Cultural and Natural Heritage.

To date a little over 33% of initial zoning has been completed for the 344 000 square kilometre area that comprises the Marine Park, making it the world's biggest and most significant marine conservation project.

The Great Barrier Reef is unique and the commitment of the Australian people to its conservation is great. This commitment has led to the establishment of legislation and a management system in which conservation is the dominant theme, with reasonable use of the Reef's resources being encouraged.

The Aquarium is part of the Wonderland Project that was conceived by the Authority's chairman and built as a Bicentennial Project with the support of the Townsville community and the Commonwealth and Queensland Governments.



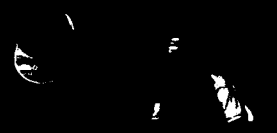
The Great Barrier Reef Marine Park Authority acts as the trustee of the Great Barrier Reef, on behalf of the people of Australia and the world.

Further information about the Great Barrier Reef Marine Park can be obtained from the Great Barrier Reef Marine Park Authority, P O Box 1379, Townsville, Queensland, Australia 4810. Telephone (077) 818811.

Great Barrier Reef Marine Park Authority

April 1989

...Ours to Use Wisely



Great Barrier Reef Marine Park Authority

The Great Barrier Reef is an irreplaceable resource, a spectacular blend of biological and physical diversity, colour, size, constant change and overall stability. It is one of the world's great natural assets — available for the use and enjoyment of all people.

In 1975 the Australian Government acted to establish a system which in many ways amounts to self regulation of the Great Barrier Reef by the people who use and depend on it, by creating the Great Barrier Reef Marine Park Authority (GBRMPA).

The GBRMPA with its main office located central to the Great Barrier Reef at Townsville in North Queensland, is responsible for managing, through the process of zoning and associated techniques, the world's largest marine park.

The Functions of the GBRMPA are:

- Planning and development of the Marine Park
- Implementing zoning and management strategies
- Research, monitoring and interpreting data
- Providing information and advice
- Operating the aquarium
- Government liaison

The Goal of the GBRMPA is —

"To provide for the protection, wise use, understanding and enjoyment of the Great Barrier Reef in perpetuity through the care and development of the Great Barrier Reef Marine Park".

The GBRMPA recognizes that

...chnology at work in planning and ...Park.

any use of the Reef or associated areas should not threaten the Reef's essential ecological characteristics and processes.

to minimizing regulation of, and interference in, human activities. It aims to protect the natural qualities of the Reef while providing for reasonable use of the Reef's resources. Provision is made for economic development consistent with the goal and other aims of the Authority.

have indicated strong support for the efforts being undertaken to care for and protect the Great Barrier Reef. It is through this community support, understanding and

The Great Barrier Reef Marine Park Authority's Townsville offices in the Wonderland complex, Townsville, Queensland.

***Research and Monitoring** — a vital aspect of the Great Barrier Reef **Marine Park Authority**'s function in managing the Marine Park.*

acceptance of the Marine Park concept that sound and effective management practices are being achieved.

is not a National Park, it is a multiple-use protected area. The main tool used in managing the Reef is zoning. Zoning separates uses that might conflict with each other, while allowing at least some space for any reasonable activity and still ensuring the protection of the Reef.

Prohibited activities in the Marine Park are oil exploration, mining (other than for approved research purposes), littering, spearfishing with SCUBA and the taking of large specimens of certain species of fish.

on public input into zoning plans. Whenever a zoning plan is about to be prepared, Reef users are invited to give their opinions on how zoning should be undertaken as well as providing information about their use of the Reef. All this information is put together, conflicts in usage are resolved, and a draft zoning plan is prepared. This draft zoning plan is then advertised and the public is again invited to comment. Changes may then be made in the draft plan before final steps are taken to make it a legal document. Each zoning plan is evaluated and revised approximately every five years.

work is a coordination of both Commonwealth and State approaches and goals in adjacent areas. The Great Barrier Reef Ministerial Council comprising four Ministers, two from each government, coordinates policy on the Reef between the Commonwealth and the Queensland governments. The Great Barrier Reef Consultative Committee, representing a wide and varied cross section of interests from both public and private sectors, advises the Authority and the Minister.

policy and guidelines, and general oversight of Marine Park management are the responsibility of the GBRMPA while the Queensland National Parks and Wildlife Service (Q.NPWS) is the principal agency responsible to the Authority for in-the-field management activity.

patrol the Reef in vessels and

Self guiding trail

Heron Island
National Park

QUEENSLAND NATIONAL PARKS AND WILDLIFE SERVICE

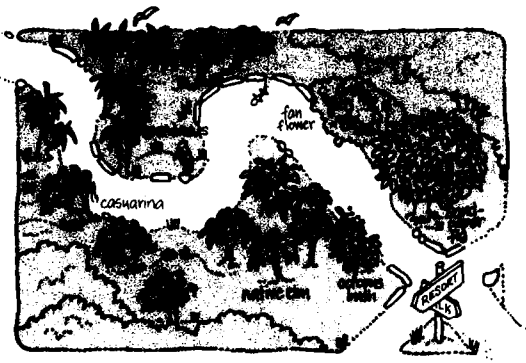
Like other cays, Heron Island is formed entirely from the remains of animals and plants that once inhabited its reef. Skeletons and rubble are crushed beneath the waves to form sediments which are accumulated by wind and water. If enough sediment is built up by this process, an unvegetated coral island (a cay) may form.

As cays grow and age, pioneer plants take hold, paving the way for less hardy species to survive. Eventually lush vegetation may flourish, forming leafy, cool forests in the interior of the cays, while pioneer plants remain on the outer, exposed edges.

Feel and smell the strong, salt-laden winds which carry fine sand upwards to form the low sandy spit which is visible from this side of the island. The she-oaks here, *Casuarina equisetifolia*, have several features enabling them to survive in this harsh environment. Exposed root galls contain nitrogen-fixing bacteria which helps survival in poor soil. Their grey-green 'leaves' are actually branchlets. Real leaves are tiny scales, reduced to restrict water loss through excess transpiration.

About 40 metres along the path to your left is a dense thicket of twiggy shrubs called *Suriana maritima*. These and other hardy shrubs help to form a wind-buffer and are tolerant to strong winds, sand-blasting, and salt-spray.

Throughout summer, the pretty yellow flowers of *Tribulus cistoides*, a low herb, may be seen at the base of pandanus palms and she-oaks which dominate this open parkland. Look for lantern bushes, *Abutilon albescans*, and native elms, *Celtus paniculata*, along here. The area is a favoured haunt of grey and white herons. You may find sacred kingfishers perched overhead. Silvereyes dart from tree to tree searching for sweet berries and fruit. Listen for the soft cooing of bar-shouldered doves as they forage in the grass.



Fan flowers, *Scaevola sericea*, and octopus bush, *Argusia argentia*, become more frequent as the path winds towards the forest. In winter, many of the island's trees and shrubs bear remnant birds nests constructed during the previous summer. Black noddies build these flimsy nests from a variety of leaves and twigs. Can you tell which trees or shrubs they prefer?

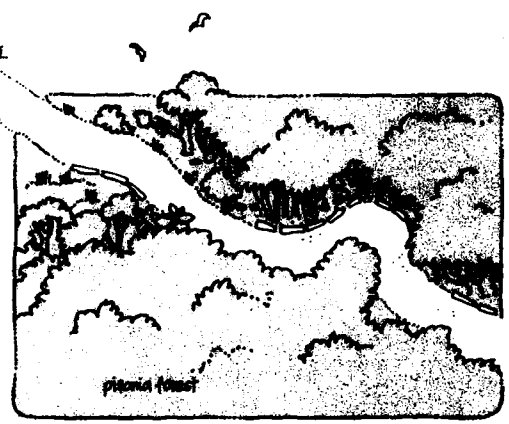
Moving further along the path, you will come to a sign-posted intersection. Just before this junction is a large sandpaper fig, *Ficus opposita*. These trees are found in open glades of the forest. Feel the rough underside of its leaves to discover how it got its name.

Venturing forth into the depths of the pisonia forest, you can see how much darker and finer the soil is compared with soil closer to the beach. Below this soil, phosphates from bird droppings may combine with humus and sand to form soft rock. Have you noticed how much cooler and more sheltered conditions are in the forest?

Can you find trees other than *Pisonia grandis* in the forest? Nearly all other plants are excluded here, leaving the sandy floor bare. Each summer, thousands of wedge-tailed shearwaters dig burrows in the forest floor and at the base of pisonia trunks. A single egg is laid at the end of each burrow and both parents rear their chick. Shearwaters depart from Heron Island at the end of summer leaving a mass of burrows.

In summer, the forest is noisy, smelly and crowded due not only to visiting shearwaters but also to thousands of black noddies nesting in the trees. Pisonia flowers are sweetly scented, small and green. Female flowers are followed by sticky, club-shaped brown fruits which can attach to nesting seabirds' feathers. Many birds die as they become bound in a sticky mass of fruit, unable to fly or feed.

At several locations along the path are fallen pisonia branches with rows of coppice shoots along their length. In fact, *Pisonia grandis* usually propagates through the rooting of fallen branches. This process provides a very effective means of advancing into the adjacent area. Quietly watch for buff-banded rails scurrying across the forest floor.



As you leave the forest and head towards the resort, we hope you take with you a new awareness of the delicate transience of the coral cay community.

QUEENSLAND NATIONAL PARKS AND WILDLIFE SERVICE

Humpback Whales on the Great Barrier Reef

Whales are the largest living animals. These marine mammals are adapted superbly to a life of swimming and diving. The humpack whale, Megaptera novaeangiae, is one of the most graceful of the great whales.

A rare species

Many experts believe humpbacks are the third most endangered whale species in the world, after the bowhead and right whales. The world population of humpbacks is approximately 10,000, only 8% of the population which existed before commercial whaling.

Migration

In the Southern Hemisphere, humpback whales spend summer in the Antarctic and in winter migrate north to breeding grounds.

One population annually migrates 5,000 kms to the Great Barrier Reef. Whales arrive in the southern Great Barrier Reef in mid June and in the following weeks they move further north to cover the entire length of the reef. Most leave reef waters by October.

Feeding

Humpback whales feed in the Antarctic in preparation for their lengthy northern migration when they abstain from feeding.

Adult humpback whales grow to an average length of about 16 metres and can weigh up to 40 tonnes. This massive bulk is supported by a diet of plankton (especially krill) and small fish. Whales sieve food from huge amounts of water through specialised fringed mouth plates made of baleen. Humpbacks therefore are known as baleen whales.

Breeding

Although providing the richest source of food, cold Antarctic waters are unsuitable for reproduction. Young whales require a warmer environment to enable them to maintain their body temperature.

Female humpback whales carry their young for 11.5 months. Members of the east Australian population apparently give birth soon after arriving in the Great Barrier Reef.

The young are 4.3 metres at birth and weigh 1.5 tonnes. Humpback whale milk has a high fat content (35% compared with 2% for human milk) and milk production can be up to 600 litres a day. On this diet, a suckling calf increases its weight five to eight times during an 11 month period. The calf develops a protective layer of blubber so that it can follow its mother back to the cold Antarctic waters.

Breathing

The first sign of whales in an area is usually the 'blow'. Air leaves the blowhole at over 400 km an hour. Whales breathe air and when they surface the exhalation of warm air produces a distinctive cloud, formed by condensation of vapour expelled from the lungs under great pressure. Adult humpbacks have two lungs, each the size of a small car, which they can empty and refill in less than two seconds.

Sound

Humpbacks are the most vocal of all great whales with their sounds ranging from high squeaks to low guttural growls. These sounds are produced by moving air back and forth through body passages. Research in various parts of the world has shown that sounds are organized into fixed sequences called 'songs'. Each sequence lasts for up to half an hour and can be repeated for hours at a time. At any given time, all singers in an area sing the same song and as the season progresses the song evolves. These haunting sounds may travel for kilometres under water and may even be heard above the surface.

The majority of the Great Barrier Reef is a marine park. Day to day management of the marine park is provided by the Queensland National Parks and Wildlife Service on behalf of the Great Barrier Reef Marine Park Authority.

For further information, contact:

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